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**Acidification of raw and co-digested pig slurries with alum before mechanical separation reduces gaseous emission during storage of solid and liquid fractions**

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*Original Citation:*

*Availability:*

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*Published version:*

DOI:10.1016/j.agee.2016.04.016

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1 **Title page**

2 **Acidification of raw and co-digested pig slurries with alum before mechanical**  
3 **separation reduces gaseous emission during storage of solid and liquid fractions**

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18 **Highlights**

19 • Acidification and separation of slurries were combined to reduce gaseous emissions

20 • Acidification reduced ammonia emissions during mechanical separation.

21 • Acidification reduces NH<sub>3</sub> and GHG emissions during storage of slurries

22 • Total GHGs from acidified fractions were lower than from non-acidified fractions.

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1 **Abstract**

2 Acidification of livestock slurries is used to reduce ammonia and methane emissions,  
3 and mechanical separation is applied to concentrate organic matter and nutrients in  
4 the resulting solid fraction (SF). The fractions obtained after separation are normally  
5 stored on farms during long periods before they can be applied to soil or transported  
6 to fields far away. During this storage period and/or transport, the emissions of  
7 ammonia and greenhouse gases (GHG) can be high, causing environmental problems.

8 The aim of this study was to assess the effects of acidification before the separation of  
9 raw and co-digested pig slurries on the gaseous emissions during the storage of the  
10 resulting liquid fraction (LF) and SF. The emission rates of  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  were  
11 followed during 70 days of storage.

12 Acidification applied before separation significantly reduced the emissions of  $\text{NH}_3$  and  
13 GHG during the storage of the fractions from raw and co-digested slurries. The main  
14 reductions were observed in the acidified fractions, relative to the non-acidified  
15 fractions (that led to the highest gaseous emissions), in both slurries. Thus,  $\text{NH}_3$  and  
16  $\text{CH}_4$  emissions were significantly reduced in acidified LFs and  $\text{N}_2\text{O}$  emissions were  
17 significantly reduced in acidified SFs. The  $\text{CO}_2$  emissions were significantly reduced in  
18 both acidified fractions from both slurries, since most of the inorganic C was released  
19 during the acidification process.

20 It can be concluded that acidification before separation is a good abatement practice  
21 to minimize ammonia emissions during separation and to reduce gaseous emissions  
22 during the storage of slurry fractions.

1 **Keywords:** Acidification; aluminum sulfate; pig slurry; co-digested slurry; mechanical  
2 separation; gaseous emissions; storage.

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## 5 **1. Introduction**

6 Large volumes of livestock slurries are produced on farms due to the intensification of  
7 livestock production (Abdalla, 2002). These slurries are normally stored in farms for  
8 several months until they can be applied to agricultural fields. During their storage,  
9 significant amounts of gaseous emissions are released to the atmosphere (Dinuccio et  
10 al., 2008).

11 Emissions of ammonia (NH<sub>3</sub>) and greenhouse gases (GHG) such as nitrous oxide (N<sub>2</sub>O),  
12 methane (CH<sub>4</sub>), and carbon dioxide (CO<sub>2</sub>), the main gases emitted from slurries  
13 (Weiske and Petersen, 2006), affect the health of humans and other animals and  
14 damage the environment (Erisman et al., 2008). Therefore, finding a proper way to  
15 reduce these emissions has become an important issue (CEC, 2005).

16 Over the past few years anaerobic co-digestion of organic substrates (such as energy  
17 crops and agro-industrial byproducts) and livestock manures has become increasingly  
18 popular in Europe. However, the output from digesters (co-digested slurry) still  
19 contains high amounts of organic matter which has not been completely degraded,  
20 leading to residual GHG emissions (Dai et al., 2013). Co-digested slurry contains also  
21 large amounts of ammonium (NH<sub>4</sub><sup>+</sup>); thus, NH<sub>3</sub> emissions also occur during storage  
22 (Sommer, 1997; Resch et al., 2008).

1 Acidification of slurries is a treatment known to reduce NH<sub>3</sub> emissions (Stevens et al.,  
2 1989; Kai et al., 2008; Fangueiro et al., 2015) and recent studies have demonstrated its  
3 capacity to reduce CH<sub>4</sub> emissions as well (Ottosen et al., 2009; Petersen et al., 2012;  
4 Wang et al., 2014). Currently, concentrated sulfuric acid is used as an acidification  
5 additive in Denmark (Eriksen et al., 2008). However, there are some concerns related  
6 to the use of this strong acid (Borst, 2001). Several studies have shown disadvantages  
7 related to its use, including excess foam formation (increasing the storage capacity  
8 required) and the pool of excess sulfur created - which can lead to significant hydrogen  
9 sulfide (H<sub>2</sub>S) emissions (Vandré and Clemens, 1997; Dai et al., 2013). Aluminum sulfate  
10 (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>), referred to hereafter as alum, is an acidifying additive which has been used  
11 successfully to reduce NH<sub>3</sub> volatilization in poultry litter (Moore et al., 1995; Sims and  
12 Luka-McCafferty, 2002). Alum is also known for its flocculant properties in wastewater  
13 treatment (Parmar et al., 2011), which suggests that it may positively affect the  
14 mechanical separation of slurry. Therefore, alum was used here as an acidifying  
15 additive to decrease the pH of raw and co-digested pig slurries.

16 Mechanical separation is currently applied in some European countries and has been  
17 widely used in Asia (Hjorth et al., 2010). It provides a liquid fraction (LF), rich in soluble  
18 N, that can be used directly on-farm as a N fertilizer, and a solid fraction (SF), rich in  
19 total solids (TS), organic matter (OM), and phosphorus, which is normally transported  
20 to other farming areas where nutrients and OM are needed (Hjorth et al., 2010).  
21 Nevertheless, previous studies (Dinuccio et al., 2008; Fangueiro et al., 2008) have  
22 demonstrated that the total amount of gaseous emissions from the separated  
23 fractions is higher than from the non-separated slurries. A recent study by Perazzolo et  
24 al. (2015) showed similar results in terms of gaseous emissions from fractions of co-

1 digested slurry, and suggested the adoption of mitigation techniques for the  
2 management of separated co-digestates. Some studies have assessed the effects of  
3 acidification of pig slurry (Dai and Blanes-Vidal, 2013; Petersen et al., 2012) and  
4 digested slurry (Wang et al., 2014) on gaseous emissions during storage, but there is  
5 no study reporting the effects on gaseous emissions during storage of the fractions  
6 obtained from acidified and separated raw and co-digested slurries.

7 We hypothesized that acidification of slurry before separation should reduce the  
8 gaseous emissions from solid and liquid fractions during storage.

9 The aim of this study was to assess the effects of the combined acidification and  
10 separation of raw and co-digested pig slurry on NH<sub>3</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O emissions  
11 during 70 days of storage.

## 12 **2. Material and methods**

### 13 **2.1 Slurry treatment**

14 Fresh pig slurry and co-digested pig slurry, with initial pH values of 7.28 and 7.85,  
15 respectively, were collected from two farms located close to Turin, Italy. The slurry  
16 samples were then kept in closed plastic barrels at 4°C for two days, before the start of  
17 the experiment.

18 Acidification was performed by adding powdered alum at a rate of 2% and 3.5% (w/w)  
19 to the untreated pig slurry (UP) and co-digested slurry (UC), respectively, to obtain  
20 acidified pig slurry (AP) and acidified co-digested slurry (AC) of pH 5.5. The acidification  
21 was performed by small additions of alum and continuous stirring, while the pH was  
22 measured with an electrode pH meter (Metrohm, Germany) until it reached a constant  
23 value of 5.5.

1 Total amounts of 86 kg, for UP and AP, or 54 kg, for UC and AC, were mechanically  
2 separated and the fractions obtained were weighed to calculate the recovery of the  
3 process. A higher amount of UP and AP was used for the separation compared to the  
4 amount of UC and AC used. The separation performance is affected by the TS content  
5 of the slurry. The TS content of UP was lower than the TS content of UC and thus, a  
6 higher amount of slurry was needed to obtain the SF required to perform the  
7 experiment. The separation was performed using a laboratory scale device described  
8 in Popovic et al. (2014), which works on the screw press principle.

## 9 **2.2 Storage conditions**

10 Acidified and non-acidified slurries and their corresponding fractions were stored in  
11 open glass vessels (5 L capacity, inner diameter 0.17 m) for 70 days under undisturbed  
12 conditions. Sample volumes of 4 L were stored in three replicates, leading to a total of  
13 36 experimental units. Each slurry sample was weighed at the beginning and end of  
14 the storage period in order to determine the weight loss during storage. Volume  
15 reductions in all the slurry samples were recorded during the storage period by  
16 measuring the increase in the headspace of the vessels. The vessels, once filled with  
17 the slurry samples, had an initial headspace of 1 L for gas measurements. The storage  
18 conditions were the same for all the samples stored. The experiment was run at  
19 ambient temperature, which was recorded by an Onset<sup>®</sup> Hobo U12 data logger during  
20 the whole storage period.

## 21 **2.3 Slurry analysis**

22 All the materials tested were analyzed at the beginning and end of the storage period  
23 for their pH, total solids (TS), volatile solids (VS), total nitrogen (TN), and total



1 ammonium ( $\text{NH}_4^+$ ) content. The TN content was analyzed by the Kjeldahl method  
2 (Horneck & Miller, 1998). The TS content was determined after drying 10 g of fresh  
3 material at  $105^\circ\text{C}$  to constant weight for 24 hours and the VS content by loss on  
4 ignition after calcination at  $550^\circ\text{C}$  for 3 hours (Clesceri et al., 1989). The total  $\text{NH}_4^+$   
5 content was analyzed after extraction with 30 mL of 0.05 M  $\text{CaCl}_2$  (van Raij, 1998;  
6 Houba et al., 2000), by segmented flow colorimetry (Skalar ScanPlus, The Netherlands).  
7 The main characteristics of the slurries at the beginning and end of the storage period  
8 are given in Tables 1 and 3.

#### 9 **2.4 Gas measurements and calculations**

10 The losses of  $\text{NH}_3$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$  were measured by the dynamic chamber method  
11 described in Berg et al. (2006).

12 The vessels were closed 30 minutes before the beginning of the measurements, using  
13 an airtight lid to create steady state conditions. The airtight lid was provided by two  
14 symmetrically situated ports for inlet and outlet air, respectively. The airflow rate into  
15 the vessels, controlled by a flowmeter, was adapted to the headspace of the vessels -  
16 to have one complete air change per minute during the whole experiment.

17 The outlet port was connected by a Teflon tube to an infrared photoacoustic analyzer  
18 (1412 Multi-gas Monitor, Innova<sup>®</sup> Air Tech Instruments, Ballerup, Denmark) for gas  
19 concentration measurements. The instrument was calibrated before the beginning of  
20 the experiment by the manufacturer and was run with corrections for cross  
21 interferences between water vapor,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  and cross compensation (Dinuccio  
22 et al., 2008). The gas concentrations at the outlet were recorded for 16 minutes, to  
23 have eight measurements for each slurry sample. Of these eight values, the first three

1 were rejected in order to have a representative measurement: the mean of the last  
2 five values recorded.

3 Gas measurements took place daily between days 1 and 8, every two days from days 8  
4 to 30, and every two days during the remaining period. Gas fluxes were calculated  
5 according to Eq. 1 as follows:

$$6 \quad F = Q \frac{(C_{out} - C_{in})}{A} \quad (\text{Eq. 1})$$

7 Where  $F$  ( $\text{mg m}^{-2} \text{h}^{-1}$ ) is the gas flux,  $Q$  is the airflow rate ( $\text{m}^3 \text{h}^{-1}$ ) dosed to the vessels,  
8  $C_{in}$  ( $\text{mg m}^{-2} \text{h}^{-1}$ ) is the gas concentration in the air inlet,  $C_{out}$  ( $\text{mg m}^{-2} \text{h}^{-1}$ ) is the gas  
9 concentration in the air outlet of the vessel, and  $A$  ( $\text{m}^2$ ) is the emitting surface area of  
10 the vessels.

11 The reduction efficiencies  $R$  (%) of the  $\text{NH}_3$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$  emissions from acidified  
12 slurries and their fractions, relative to untreated slurries (Wang et al., 2014), were  
13 calculated as follows (Eq. 2):

$$14 \quad R (\%) = 100 - \text{Relative emission} \quad (\text{Eq. 2})$$

15 where the *Relative emission* (%) is calculated as the mean value of individual gas  
16 fluxes during the whole storage period and is related to the mean values of each gas  
17 flux from untreated slurries, as follows (Eq. 3):

$$18 \quad \text{Relative emission} (\%) = \frac{F_{\text{Acidified slurry}}}{F_{\text{Untreated slurry}}} \times 100 \quad (\text{Eq. 3})$$

19 The cumulative emissions ( $\text{mg vessel}^{-1}$ ) for each gas during the whole storage period  
20 were calculated by the mean values between two sampling events multiplied by the  
21 time interval between them, as described in Fangueiro et al. (2008). The cumulative

1 carbon (CH<sub>4</sub> and CO<sub>2</sub>) and nitrogen (NH<sub>3</sub> and N<sub>2</sub>O) emissions were expressed as  
2 percentages (%) of the respective initial volatile solids (VS) and total nitrogen (TN)  
3 content in each slurry and fraction.

4 To study the effect of the separation process on gaseous emissions, the sum of the  
5 corrected cumulative emissions from acidified and non-acidified separated fractions  
6 were compared with their respective unseparated slurries. The sum of the emissions  
7 was calculated (Eq. 4) as follows:

$$8 \quad E_T = X_{LF} \cdot E_{LF} + X_{SF} \cdot E_{SF} \quad (\text{Eq. 4})$$

9 where  $E_T$  is the sum of the corrected cumulative emissions from separated slurries,  
10  $E_{LF}$  and  $E_{SF}$  are the corrected cumulative emissions for liquid and solid fractions,  
11 respectively, and  $X_{LF}$  and  $X_{SF}$  are the proportions of liquid and solid fractions,  
12 respectively, obtained after separation of acidified and non-acidified slurries.

13 To assess the global warming potential (GWP) of each treatment, the N<sub>2</sub>O and CH<sub>4</sub>  
14 cumulative emissions were converted to CO<sub>2</sub> equivalents by using their respective  
15 GWPs. According to IPCC (2013), in a 100-year time horizon, the GWP values are 298  
16 and 25 for N<sub>2</sub>O and CH<sub>4</sub>, respectively. For NH<sub>3</sub> emissions, the value is estimated to be  
17 1% of the deposited N<sub>2</sub>O (de Vries et al., 2011).

## 18 **2.5 Statistical analysis**

19 All the data obtained were analyzed by analysis of variance (one-way ANOVA). The  
20 statistical significance of the differences among the means was determined by a Tukey  
21 test at P<0.05. The statistical software package used was STATISTIX 7.0 (Analytical  
22 Software, Tallahassee, FL).

### 1 **3. Results and discussion**

#### 2 **3.1 Initial slurry characteristics**

3 The main characteristics of the slurries at the beginning of the storage period are given  
4 in Table 1. Untreated raw pig slurry (UP) had a significantly ( $P<0.05$ ) lower initial pH  
5 (7.28) than untreated co-digested (UC) slurry (pH 7.85). Therefore, less alum was  
6 required to lower the pH to 5.5 in raw (2% w/w) than in co-digested slurry (3.5% w/w).

7 The total solids (TS) content was significantly ( $P<0.05$ ) higher in UC (55.2 g kg<sup>-1</sup> slurry)  
8 than in UP (45.9 g kg<sup>-1</sup> slurry) and both increased significantly ( $P<0.05$ ) with  
9 acidification by 64% and 33%, respectively. This increase in TS was previously observed  
10 by Eriksen et al. (2008), Kai et al. (2008), and Fangueiro et al. (2009) and was attributed  
11 to the sulfate added with the acid. The increase in TS promoted by acidification was  
12 transferred to the acidified liquid fractions (ALFs) when separation was applied: higher  
13 TS concentrations were observed in the ALFs from both slurries, relative to the  
14 untreated LFs, while a decrease in TS was observed in the ASFs, relative to the SFs,  
15 from both slurries (Table 1). A recent study by Hjorth et al. (2015) reported that  
16 hydrolysis is accelerated by acidification; thus, the increase in TS (and in the  
17 corresponding total VS content) in the ALF was probably due to an increase in low  
18 molecular weight carbohydrates derived from cellulose or hemicellulose present in the  
19 LF of the slurries.

20 The total nitrogen (TN) content was significantly ( $P<0.05$ ) higher in UC (57.9 g kg<sup>-1</sup> TS)  
21 than in UP (53.7 g kg<sup>-1</sup> TS) and in both cases was not affected by acidification. The TN  
22 concentration was significantly ( $P<0.05$ ) decreased by acidification (on a dry weight  
23 basis). However, the reduction in TN concentration was mainly due to the increase in

1 the TS content and was not significant when considering the concentration on a wet  
2 weight basis (Table 1).

3 The total ammonium nitrogen (TAN) content was also significantly ( $P < 0.05$ ) higher in  
4 UC ( $40.1 \text{ g kg}^{-1}$  TS) than in UP ( $35.5 \text{ g kg}^{-1}$  TS) and, in both cases, was increased by  
5 acidification compared to untreated slurries (Table 1).

## 6 **3.2 Gaseous emissions during storage**

### 7 **3.2.1 NH<sub>3</sub> emissions**

8 For the raw pig slurry, ammonia (NH<sub>3</sub>) emissions occurred mainly from the untreated  
9 slurry (UP) and from its derived LF, and both followed the same trend (Fig. 1a). The  
10 emissions started to rise from the beginning of the storage - to reach a peak of  $170 \text{ mg}$   
11  $\text{NH}_3 \text{ m}^{-2} \text{ h}^{-1}$  at day 41 for UP and of  $198 \text{ mg NH}_3 \text{ m}^{-2} \text{ h}^{-1}$  at day 30 for the P-LF, slightly  
12 decreasing afterwards until the end of the storage (Fig. 1a). These NH<sub>3</sub> emissions  
13 accounted for losses of 18.8% (UP) and 25.7% (P-LF) of the initial N content and losses  
14 of 31.9% (UP) and 39.2% (P-LF) of the initial TAN content (Table 2).

15 Untreated co-digested slurry (UC) and its fractions followed a different trend - relative  
16 to raw slurry - regarding NH<sub>3</sub> emissions, with C-LF and C-SF showing the highest  
17 emissions (Fig. 1b). The C-LF showed a gradual increase during the first 2 weeks,  
18 reaching a peak ( $157 \text{ mg NH}_3 \text{ m}^{-2} \text{ h}^{-1}$ ) at day 30 before slightly decreasing until the end  
19 of the storage. In contrast, the emissions from UC and C-SF were highest during the  
20 first week and showed a gradual decrease from the beginning of the storage, reaching  
21 undetectable values after 4 and 3 weeks, respectively. The UC showed values that  
22 were always under  $50 \text{ mg NH}_3 \text{ m}^{-2} \text{ h}^{-1}$  and C-SF had the highest peak ( $116 \text{ mg NH}_3 \text{ m}^{-2}$   
23  $\text{h}^{-1}$ ) at day 3 (Fig. 1b), decreasing drastically afterwards. The highest NH<sub>3</sub> emissions

1 observed from C-LF and C-SF accounted for a total N loss of 18.5% and 9.8% of the  
2 initial N content and a total loss of 30.8% and 26.6% of the initial TAN content,  
3 respectively (Table 2).

4 The main differences observed regarding NH<sub>3</sub> emissions between raw and co-digested  
5 slurry can be attributed to the initial slurry characteristics (Table 1). Besides the  
6 chemical composition, the co-digested slurry originated from an anaerobic digester fed  
7 with 67% pig slurry, 23% maize and triticale silage, and 10% farmyard manure and  
8 cattle slurry. Undigested silage may explain the higher content of large particles in the  
9 co-digested slurry, in comparison with the raw slurry. These particles normally have a  
10 high content of cellulose and lignin; therefore, there may have been less C readily  
11 available for degradation than in the raw slurry and thus, less mineral N should be  
12 immobilized by microorganisms. To verify this statement, VS losses during storage  
13 were calculated by mass balances using the initial and final analyses of the slurries  
14 (Tables 1 and 3). The decrease in the VS content was greater in raw (41%) than in co-  
15 digested slurry (22%), confirming that the catabolic activity was higher in the raw pig  
16 slurry. The decarboxylation of organic acids consumes protons and raises the pH, with  
17 the corresponding release of NH<sub>3</sub> (Petersen et al., 2012). The raw slurry, after the 70-d  
18 storage, had undergone a greater increase in pH than the co-digested slurry (Table 3) -  
19 another indicator giving support to previous findings.

20 Previous studies showed that the initial slurry characteristics affect the separation  
21 performance of the slurry (Møller et al., 2002). Thus, the differences observed in the  
22 NH<sub>3</sub> volatilization of the LFs and SFs from both slurries can be attributed to the initial  
23 composition of the fractions. As explained before, the co-digested slurry had larger

1 particles, which were transferred to the SF. The P-SF was more compacted than the C-  
2 SF and thus had a higher density ( $563 \text{ kg m}^{-3}$ ) than the C-SF ( $300 \text{ kg m}^{-3}$ ). The lower  
3 density of the C-SF may be related to the high content of straw in the co-digestate,  
4 which was transferred to the SF. Straw normally contains high amounts of lignin and  
5 cellulose, which are not readily degradable by microorganisms (Hansen et al., 2006).  
6 Thus, microbial activity should be lower and immobilization of ammonium may be  
7 minimal, allowing  $\text{NH}_3$  release.

8 Acidification of slurries reduced  $\text{NH}_3$  emissions drastically during the whole storage  
9 period, with values always below 33 and  $11 \text{ mg NH}_3 \text{ m}^{-2} \text{ h}^{-1}$  in acidified raw pig slurry  
10 (AP) and co-digested slurry (AC), respectively (Fig. 1).

11 The mean  $\text{NH}_3$  reduction efficiencies obtained by acidifying raw and co-digested  
12 slurries were 92% and 70%, respectively, relative to the non-acidified slurries. The  
13 acidified fractions from raw slurry, AP-LF and AP-SF, showed reductions of 78% and  
14 31%, respectively, while 96% reductions were observed for both fractions of the  
15 acidified co-digested slurry, AC-LF and AC-SF.

16 The reductions in  $\text{NH}_3$  emissions obtained in our study were greater than those of  
17 previous studies where sulfuric acid was used as the acidifying additive. Dai and  
18 Blanes-Vidal (2013) obtained a reduction of 77% when lowering the pH of pig slurry to  
19 5.5 and Wang et al. (2014) observed a daily mean reduction of 40.2% for acidified  
20 digested slurry. These differences may be partially due to the initial higher TS content  
21 of the acidified slurries in our study (Vaddella et al., 2013). According to De Visscher et  
22 al. 2002 the adsorption of  $\text{N-NH}_4^+$  on suspended organic solids reduces the diffusion  
23 coefficient resulting in lower  $\text{NH}_3$  volatilization. In addition, at the end of the storage

1 period in our study, the acidified slurries had pH values lower than the initial pH of the  
2 non-acidified slurries (and lower than the values in previous studies), meaning that a  
3 low and stable pH was maintained in the acidified slurries during storage. This was  
4 probably due to the use of alum, which - in contrast to sulfuric acid - should not be  
5 buffered so fast and therefore CO<sub>2</sub> emissions and the consequent NH<sub>3</sub> release should  
6 be lower. The NH<sub>3</sub> emissions from acidified slurries in our study showed a slight  
7 increase after week 2, while the acidified slurries in Dai and Blanes-Vidal (2013) and in  
8 Wang et al. (2014) had a faster and higher increase in NH<sub>3</sub> emissions; these differences  
9 explain, as well, the higher reduction efficiencies obtained in our study.

10 Previous studies by Dinuccio et al. (2008) and Fangueiro et al. (2008) have shown NH<sub>3</sub>  
11 emissions to increase when raw slurry is separated. The same findings were observed  
12 by Perazzolo et al. (2015) when separating co-digested slurry. This increase was mainly  
13 due to high NH<sub>3</sub> volatilization from the LF. Vaddella et al. (2013) demonstrated a higher  
14 degree of NH<sub>3</sub> volatilization when the TS content decreased. When acidification was  
15 applied in our study, a higher TS content was obtained in the LFs and, thus, NH<sub>3</sub>  
16 volatilization was lower. Therefore, the NH<sub>3</sub> emissions from the separated fractions  
17 together were less than from untreated slurries.

### 18 **3.2.2 N<sub>2</sub>O emissions**

19 Nitrous oxide (N<sub>2</sub>O) emissions are a byproduct of the nitrification/denitrification  
20 process which occurs when both aerobic and anaerobic conditions coexist in manure  
21 (Loyon et al., 2007). According to the measured N<sub>2</sub>O emissions, such conditions only  
22 appeared in the SFs from both slurries and in the untreated co-digested (UC) slurry. In  
23 the remaining samples, N<sub>2</sub>O emissions during the 70-day storage period were minimal,



1 as the conditions were mainly anaerobic (Fig. 2). Emissions of N<sub>2</sub>O from the P-SF  
2 occurred between days 6 and 23 of the storage, reaching a peak (351 mg N<sub>2</sub>O m<sup>-2</sup> h<sup>-1</sup>)  
3 at day 8 (Fig. 2a). These results are in agreement with previous studies by Dinuccio et  
4 al. (2008) and can be attributed to the aerobic conditions and lower moisture content  
5 of the SFs.

6 The C-SF showed lower N<sub>2</sub>O emission rates than P-SF, reaching a peak at day 41 (47 mg  
7 N<sub>2</sub>O m<sup>-2</sup> h<sup>-1</sup>). At day 16 the emission started to decrease, until the end of the storage.  
8 Untreated co-digested slurry had a high content of straw, which was displaced towards  
9 the surface of the vessel during the storage due to its lower density in relation to the  
10 liquid. This straw dried out with time due to water evaporation and acted as a surface  
11 crust, with some aerobic zones in between the anaerobic parts. Therefore, the  
12 nitrification/denitrification process, and thus the N<sub>2</sub>O release, may have taken place  
13 here. In agreement with our results, previous studies (Sommer et al., 2000; Berg et al.,  
14 2006) found N<sub>2</sub>O production only when a dry crust was present on the slurry. In our  
15 study this crust became drier with time - which may explain why the N<sub>2</sub>O emissions  
16 started at day 27 in UC. The N<sub>2</sub>O emission reached its peak at day 41 (32 mg N<sub>2</sub>O m<sup>-2</sup> h<sup>-1</sup>)  
17 <sup>1</sup>), decreasing afterwards until the end of storage (Fig. 2b).

18 The decrease of the TAN content during storage was greater than that of the TN  
19 content in P-SF, C-SF, and UC, indicating that some NH<sub>4</sub><sup>+</sup> may have been nitrified during  
20 storage - leading to N<sub>2</sub>O release. It is of note that the NH<sub>3</sub> emissions decreased as the  
21 proportion of oxidized NH<sub>4</sub><sup>+</sup> increased. The emission of NH<sub>3</sub> dropped when the N<sub>2</sub>O  
22 emission started to rise: at days 6 and 20 in P-SF and C-SF, respectively, and at day 27  
23 in UC.

1 The cumulative emission of N<sub>2</sub>O accounted for a loss of 9.2% and 6.6% of the initial  
2 total N content in P-SF and C-SF, respectively (Table 2). Dinuccio et al. (2008) observed  
3 a lower N<sub>2</sub>O emission rate in the SF from pig slurry and a corresponding lower  
4 percentage loss of N. This may have been due to a higher density of the SF in our  
5 study, which limits NH<sub>3</sub> emission and increases the proportion of the NH<sub>4</sub><sup>+</sup> content  
6 undergoing nitrification (Hansen et al., 2006). The N<sub>2</sub>O emissions from UC accounted  
7 for a loss of 1.6% of the initial N content (Table 2). The N<sub>2</sub>O emission rate from C-SF  
8 was much lower than in P-SF; so, the high percentage loss of N from C-SF was due to  
9 the lower initial N content, as this fraction had a lower density than P-SF (Table 1).

10 Acidification inhibited N<sub>2</sub>O emissions, during the whole storage period, from the SFs of  
11 both slurries and untreated co-digested slurry (Fig. 2). Acidification may have inhibited  
12 the nitrification/denitrification process, as N<sub>2</sub>O emissions were significantly reduced  
13 and nitrate was not detected in acidified slurries at the end of the storage. Accordingly,  
14 previous studies reported a delay/decrease of nitrification in acidified slurry following  
15 soil application (Fangueiro et al., 2013). The mean reduction efficiencies for N<sub>2</sub>O were  
16 91% and 95% for UC and C-SF, respectively, and 88% for P-SF.

### 17 **3.2.3 CO<sub>2</sub> emissions**

18 The emission rates of carbon dioxide (CO<sub>2</sub>) showed high variability during the whole  
19 storage period, with the highest rates observed in the first three weeks of storage (Fig.  
20 3). Significantly higher emissions of CO<sub>2</sub> were observed from P-SF and C-SF, which  
21 peaked at days 6 (8921 mg CO<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup>) and 20 (7232 mg CO<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup>), respectively,  
22 before decreasing to values lower than 2000 mg CO<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup> at day 30. The cumulative  
23 CO<sub>2</sub> emissions from the SFs accounted for a total C loss (present in the initial VS

1 content) of 19.3% and 17.2% of the initial C content in P-SF and C-SF, respectively  
2 (Table 2).

3 The CO<sub>2</sub> emissions are related to the amount of C present in the slurries (Fangueiro et  
4 al., 2008); thus, fractions with a higher C content have higher CO<sub>2</sub> emission rates. In  
5 accordance with this, the SFs in our study which had a higher C content (Table 1) were  
6 the ones showing higher CO<sub>2</sub> emissions. In addition, SFs have greater aeration relative  
7 to untreated slurries and LFs, which results in higher aerobic microbial activity.

8 The two main sources of CO<sub>2</sub> emission are the microbial degradation of organic matter  
9 and urea mineralization (Moset et al., 2012). The high CO<sub>2</sub> release from C-SF during the  
10 first three weeks of storage could have been due to these two processes, but also to a  
11 higher rate of organic N mineralization. This organic N transformation is accompanied  
12 by NH<sub>3</sub> volatilization which, as shown before (Fig. 1b), was significant during the first  
13 three weeks. The CO<sub>2</sub> emissions dropped after 30 days in the SFs from both slurries,  
14 probably due to depletion of the easily degradable C. In addition, the reduction of  
15 slurry volume due to water evaporation and sample compaction diminishes the  
16 aerobic nature of the conditions, which consequently reduces the microorganism-  
17 mediated aerobic degradation.

18 Acidification significantly ( $P < 0.05$ ) reduced the CO<sub>2</sub> emissions from both slurries and  
19 fractions, except from day 30 onwards - when acidified SFs showed higher CO<sub>2</sub> values  
20 than non-acidified SFs (Fig. 3). The mean reduction efficiencies for CO<sub>2</sub> were 48% and  
21 54% for AP and AC, respectively, 48% and 70% for AP-LF and AC-LF, respectively, and  
22 41% and 46% for AP-SF and AC-SF, respectively. Most of the dissolved CO<sub>2</sub> is lost  
23 during the acidification process (Fangueiro et al., 2008); therefore, the high reduction

1 in CO<sub>2</sub> emissions during the storage of acidified slurries was partly due to this process.  
2 However, the maintenance of low CO<sub>2</sub> emissions during storage also affects the NH<sub>3</sub>  
3 volatilization - which, as shown before, was significantly reduced during the storage of  
4 acidified slurries.

### 5 **3.2.4 CH<sub>4</sub> emissions**

6 Methane (CH<sub>4</sub>) is released from slurry as a consequence of C degradation in anaerobic  
7 conditions (Hansen et al., 2006). Methane emissions were mainly observed in the  
8 untreated slurries and LFs from both slurries, with higher rates in raw than in co-  
9 digested pig slurry (Fig. 4). This, as explained before, was due to the higher level of  
10 readily degradable C present in raw slurry, relative to co-digested slurry, as most of the  
11 easily degradable matter in co-digested slurry had been lost during the anaerobic  
12 digestion (Perazzolo et al., 2015).

13 Methane emissions from UP started to rise from the beginning of the storage, reaching  
14 peaks at days 20 (641 mg CH<sub>4</sub> m<sup>-2</sup> h<sup>-1</sup>) and 34 (522 mg CH<sub>4</sub> m<sup>-2</sup> h<sup>-1</sup>) before decreasing to  
15 values < 50 mg CH<sub>4</sub> m<sup>-2</sup> h<sup>-1</sup> from day 37 (Fig. 4a). The P-LF and P-SF followed the same  
16 trend, with a peak of 743 mg CH<sub>4</sub> m<sup>-2</sup> h<sup>-1</sup> for P-LF and of 340 mg CH<sub>4</sub> m<sup>-2</sup> h<sup>-1</sup> for P-SF, in  
17 both cases on day 13 (Fig. 4a). These CH<sub>4</sub> emissions accounted for a loss (as a % of the  
18 C present in the initial VS content) of 5.8%, 13.2%, and 1% of the initial C content in  
19 UP, P-LF, and P-SF, respectively (Table 2). This C loss as CH<sub>4</sub> is in accordance with the  
20 values observed by Dinuccio et al. (2008) for pig slurry stored at 25°C, this temperature  
21 being the mean temperature also registered in our study over the whole storage  
22 period.

1 The CH<sub>4</sub> emissions from UC and C-LF showed high variability during storage, following  
2 the same trend as raw pig slurry, and the values for C-SF were negligible (Fig 4b). A  
3 slight increase in the CH<sub>4</sub> emissions from UC and C-LF was observed at the beginning of  
4 storage, reaching a peak at day 20 in both UC (125 mg CH<sub>4</sub> m<sup>-2</sup> h<sup>-1</sup>) and C-LF (95 mg CH<sub>4</sub>  
5 m<sup>-2</sup> h<sup>-1</sup>) and slightly decreasing afterwards until the end of the storage (Fig. 4b). The  
6 cumulative CH<sub>4</sub> emissions in both cases accounted for less than 2% of the total initial C  
7 content (Table 2).

8 Acidification may alter methanogenic activity, as the process is normally inhibited at  
9 pH values below 6 (Weiland, 2010). Acidification reduced the CH<sub>4</sub> emissions from both  
10 slurries and fractions (Fig. 4), with mean reduction efficiencies of 81% and 92% for AP  
11 and AP-LF, respectively. The mean CH<sub>4</sub> emissions were reduced in AC and AC-LF, by  
12 91% in both cases. Wang et al. (2014) observed a mean CH<sub>4</sub> reduction efficiency of  
13 80.8% when acidifying digested pig slurry to pH 5.5. This small difference in reduction  
14 efficiencies could be due to the different timeframe in the calculation by Wang et al.  
15 (2014), as they only considered the first 20 days of storage while we considered the  
16 whole period (70 days). However, our reduction efficiencies closely resemble the  
17 values observed by Petersen et al. (2014), who found that CH<sub>4</sub> emissions were reduced  
18 by 94% when pig slurry was acidified during storage.

### 19 **3.3 Effect of the combined acidification and separation on GHG emissions**

20 To assess the effects of acidification applied before separation on net total GHG  
21 emissions, the global warming potential (GWP) for each gas was considered in order to  
22 express an overall effect in terms of CO<sub>2</sub> equivalents (Fig. 5).

1 Separation alone significantly increased the net total GHG emissions of the solid and  
2 liquid fractions (combined together): by 48% for raw slurry and by 5% for co-digested  
3 slurry, relative to the untreated slurries (Fig. 5). The increment observed when raw pig  
4 slurry was separated was mainly due to the increase in N<sub>2</sub>O emissions from SF, the  
5 increase in CH<sub>4</sub> emissions from LF, and the increase in CO<sub>2</sub> emissions from both LF and  
6 SF (Fig. 5). This is in accordance with previous results obtained by Dinuccio et al.  
7 (2008), where the combined emissions from separated fractions were always higher  
8 than from unseparated slurries. However, when acidification was applied before  
9 separation, the net total GHG emissions of the acidified fractions combined together  
10 were significantly lower than from untreated slurries.

11 Reductions in the net total GHG emissions of 59% and 81% were observed for the sum  
12 of the acidified fractions from raw and co-digested slurry, respectively, relative to  
13 untreated slurries. The reductions for acidified raw slurry were mainly due to the  
14 lower CH<sub>4</sub> loss from the acidified LF and to the lower loss of N<sub>2</sub>O from the acidified SF,  
15 relative to the corresponding non-acidified fractions. The decrease for co-digested  
16 slurry was mainly due to the undetectable values of N<sub>2</sub>O and CH<sub>4</sub> for acidified SF and  
17 LF, respectively, and to the smaller loss of CO<sub>2</sub> from both acidified fractions, relative to  
18 the corresponding non-acidified fractions (Fig. 5).

19 Therefore, acidification of slurry before separation can be considered a good  
20 abatement option to decrease net total GHG emissions during the storage of fractions  
21 from both raw and co-digested pig slurries.

### 22 **3.4 Final slurry characteristics**

1 The main characteristics of the slurries at the end of the storage period are given in  
2 Table 3.

3 After 70 days of storage, all sample volumes were reduced due to water evaporation  
4 and organic matter degradation. The weight loss ranged from 0.5 kg to 1.4 kg, with  
5 greater losses in the LFs (Table 3). The TS content decreased during storage: by 33%  
6 and 14% in UP and UC, respectively. The VS content followed the same trend, with a  
7 reduction of 41% and 22% in UP and UC, respectively. However, acidified slurries had  
8 lower decreases in both the TS and VS contents: AP only showed a 5.2% decrease in TS  
9 and 11% in VS, and AC maintained the same initial TS content and had a small  
10 reduction of 3% in its VS content. The acidified LFs from both slurries followed the  
11 same trend in terms of TS and VS content as their respective acidified slurries, while  
12 the acidified SFs showed lower TS and VS reductions relative to the untreated SFs.  
13 Microbial degradation is reduced upon acidification (Hjorth et al., 2015), by inhibition  
14 of acidogenesis, acetogenesis, and methanogenesis. However, our results show that  
15 some microbial degradation may still have occurred in the acidified slurries during  
16 storage, as the final values of TS and VS were lower than their initial values.

17 After storage, the TN and TAN concentrations of the pig and co-digested slurries had  
18 significantly decreased, with PS and CS and their respective LFs showing the highest N  
19 losses (Table 3). The N losses were 68% and 40% in the PS and CS slurry, respectively,  
20 which are mainly attributable to  $\text{NH}_3$  volatilization as the TAN values were reduced by  
21 88% and 50%, respectively.

22 The same trend was followed by the LFs from both slurries, with TN losses of 77% and  
23 65% from P-LF and C-LF, respectively. These fractions showed an almost complete loss

1 of TAN: 95% and 86% in P-LF and C-LF, respectively. These results are in agreement  
2 with the studies by Perazzolo et al. (2015) and Fangueiro et al. (2008), where the losses  
3 were highest in the LFs because they had the highest TAN:TN ratios and low TS  
4 contents.

5 The N losses from the SFs may have been due partially to  $\text{NH}_3$  volatilization but also to  
6 some immobilization and/or nitrification of the TAN. The TN in the SFs declined by 43%  
7 and 35% and the TAN by 96% and 92% in P-SF and C-SF, respectively. Some  
8 immobilization may have occurred in these SFs, promoted by their high C:N ratios. On  
9 the other hand, nitrate ( $\text{NO}_3^-$ ) was detected in the C-SF at the end of the storage,  
10 confirming that some nitrification may have occurred as well. Nitrification is known to  
11 occur in the SF as the oxygenation is allowed so aerobic conditions between particles  
12 occur (Hansen et al., 2006). The C-SF was less compacted than the P-SF due to the  
13 larger particles present in the co-digested slurry. Thus, the aeration was probably  
14 greater, promoting the nitrification process.

15 Relative to the non-acidified slurries and their fractions, acidification maintained  
16 higher total N contents during storage. Also, acidification may have promoted  
17 mineralization of organic N in AP and in the acidified LFs from both slurries, as the  
18 increase in TAN was higher than the increase in total N, relative to the non-acidified  
19 pig slurry and LFs. However, some immobilization and/or nitrification may have  
20 occurred in acidified co-digested slurry and in the acidified SFs from both slurries, as  
21 the increase in total N was higher than the increase in TAN, relative to the non-  
22 acidified co-digested slurry and SFs.

#### 23 **4. Conclusions**



1 The following conclusions relate to the results obtained with the particular slurries,  
2 and under the specific conditions, described previously.

3 Our results show that acidification of slurries with alum before separation reduces  
4 gaseous emissions from the solid and liquid fractions during their subsequent storage.

5 Acidification of pig and co-digested slurries reduces the loss of TS and VS during  
6 storage, compared to non-acidified slurries. This indicates that microbial degradation is  
7 decreased by acidification and, thus, more organic matter remains in the slurries at the  
8 end of storage. Furthermore, the TAN concentration is significantly reduced in  
9 untreated slurries during storage - due to  $\text{NH}_3$  volatilization, immobilization, and/or  
10 nitrification - but only slightly decreased in acidified slurries and fractions. Therefore,  
11 acidified slurries and their fractions have a higher fertilizing value, as less N and organic  
12 matter is lost via volatilization and microbial degradation.

13 Acidification before separation increases the TS and TAN contents in acidified LFs from  
14 both types of slurry assayed here, relative to non-acidified LFs, indicating that  $\text{NH}_3$   
15 volatilization decreases during separation.

16 Acidification of pig and co-digested slurries significantly reduces the emissions of  $\text{NH}_3$ ,  
17 particularly in the acidified LF, relative to non-acidified fractions.

18 The highest contribution of the gaseous emissions from the untreated pig and co-  
19 digested fractions to the total GHG corresponds to  $\text{CH}_4$  from LFs and  $\text{N}_2\text{O}$  from SFs, and  
20 these emissions are higher from raw pig slurry than from co-digested fractions. When  
21 acidification is applied, emissions of both  $\text{CH}_4$  and  $\text{N}_2\text{O}$  are drastically reduced, with co-  
22 digested slurry having higher proportional decreases than pig slurry. However, as the

1 total GHG emissions from pig slurry are higher than from co-digested slurry, the  
2 reduction in the total gaseous emission is also higher.

3 Mechanical separation increases the net total gaseous emissions during the storage of  
4 the separated fractions, relative to unseparated slurries. However, if acidification is  
5 applied before separation, the sum of the gaseous emissions from both acidified  
6 fractions is significantly lower than the sum of the non-acidified fractions. Moreover,  
7 the sum of the gaseous emissions from the acidified SF and LF is also lower than for  
8 the unseparated acidified slurries.

9 Acidification applied before separation, as a mitigation practice, can lead to the overall  
10 improvement of management practices on farms. It decreases the net total GHG and  
11 NH<sub>3</sub> emissions during storage of raw and co-digested pig slurry fractions. More N  
12 remains in the slurries, increasing their fertilizer value while reducing environmental  
13 pollution and protecting the health of farmers and animals. However, further studies  
14 would be required to assess the concentration of alum used in slurries if these are  
15 intended to be used as fertilizer.

16 The gas measurements in this study were made under laboratory conditions. Farm-  
17 scale measurements should be carried out in order to confirm these promising results.

## 18 **Acknowledgements**

19 The research leading to these results has received funding from the People Programme  
20 (Marie Curie Actions) of the European Union's Seventh Framework Program FP7/2007-  
21 2013/under REA grant agreement n° [289887]. This document reflects only the  
22 author's view and the Union is not liable for any use that may be made of the

1 information contained therein. The authors thank Luca Rollé and Dalibor Cuk for their  
2 valuable and outstanding technical support.

### 3 **5. References**

4 Abdalla, C. W., 2002. The Industrialization of Agriculture: Implications for Public  
5 Concern and Environmental Consequences of Intensive Livestock Operations. Penn St.  
6 Environ. Law Rev. 10, 175-191.

7 Berg, W., Brunsch, R., Pazsiczki, I., 2006. Greenhouse gas emissions from covered slurry  
8 compared with uncovered during storage. Agric. Ecosyst. Environ. 112, 129-134.

9 Borst, G.H.A., 2001. Acute intoxication of pigs with hydrogen sulphide as a result of  
10 acidification of slums. Tijdschr Diergeneeskd. 126, 104–105.

11 CEC, 2005. Communication from the Commission to the Council and the European  
12 Parliament on a Thematic Strategy on Air Pollution.

13 Dai, X.R., & Blanes-Vidal, V., 2013. Emissions of ammonia, carbon dioxide, and  
14 hydrogen sulfide from swine wastewater during and after acidification treatment:  
15 effect of pH, mixing and aeration. J. Environ. Manage. 115, 147-154.

16 De Visscher, A., Harper, L.A., Westerman, P.W., Liang, Z., Arogo, J., Sharpe, R.R., Van  
17 Cleemput, O., 2002. Ammonia emissions from anaerobic swine lagoons: model  
18 development. J. Appl. Meteor. 41, 426-433.

19 De Vries, W., Kros, J., Reinds, G.J., Butterbach-Bahl, K., 2011. Quantifying impacts of  
20 nitrogen use in European agriculture on global warming potential. Curr. Opin. Environ.  
21 Sustain. 3, 291-302.

1 Dinuccio, E., Berg W., Balsari P., 2008. Gaseous emissions from the storage of  
2 untreated slurries and the fractions obtained after mechanical separation. *Atmos.*  
3 *Environ.* 42, 2448–2459.

4 Eriksen, J., Sorensen, P., Elsgaard, L., 2008. The fate of sulfate in acidified pig slurry  
5 during storage and following application to cropped soil. *J. Environ. Qual.* 37, 280-286.

6 Erisman, J.W., Bleeker, A., Hensen, A., Vermeulen, A., 2008. Agricultural air quality in  
7 Europe and the future perspectives. *Atmos. Environ.* 42, 3209-3217.

8 Fangueiro, D., Coutinho, J., Chadwick, D., Moreira, N., Trindade, H., 2008. Effect of  
9 cattle slurry separation on greenhouse gas and ammonia emissions during storage. *J.*  
10 *Environ. Qual.* 37, 2322-2331.

11 Fangueiro, D., Surgy, S., Coutinho, J., Vasconcelos, E., 2013. Impact of cattle slurry  
12 acidification on carbon and nitrogen dynamics during storage and after soil  
13 incorporation. *J. Plant Nutr. Soil Sci.* 176, 540–550

14 Fangueiro, D., Hjorth, M., Gioelli, F., 2015. Acidification of animal slurry – A review. *J.*  
15 *Environ. Manage.* 149, 46-56.

16 IPCC, 2013. *Climate Change 2013: The Physical Science Basis. Contribution of Working*  
17 *Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate*  
18 *Change.* Cambridge University Press, Cambridge, United Kingdom and New York, NY,  
19 USA.

20 Hansen, M.N., Henriksen, K., Sommer, S.G., 2006. Observations of production and  
21 emission of greenhouse gases and ammonia during storage of solids separated from  
22 pig slurry: Effects of covering. *Atmos. Environ.* 40, 4172-4181.

1 Hjorth, M., Christensen, K. V., Christensen, M. L., Sommer, S. G., 2010. Solid-liquid  
2 separation of animal slurry in theory and practice: A review. *Agron. Sustain. Dev.* 30,  
3 153-180.

4 Hjorth, M., Cocolo, G., Jonassen, K., Abildgaard L., Sommer, S., 2015. Continuous in-  
5 house acidification affecting animal slurry composition. *Biosyst. Eng.* 132, 56-60.

6 Kai, P., Pedersen P., Jensen J.E., Hansen M.N., Sommer S.G., 2008. A whole-farm  
7 assessment of the efficacy of slurry acidification in reducing ammonia emissions. *Eur. J.*  
8 *Agron.* 28, 148–154.

9 Loyon, L., Guiziou, F., Beline, F., Peu, P., 2007. Gaseous emissions (NH<sub>3</sub>, N<sub>2</sub>O, CH<sub>4</sub> and  
10 CO<sub>2</sub>) from the aerobic treatment of piggery slurry-Comparison with a conventional  
11 storage system. *Biosyst. Eng.* 97, 472-480.

12 Moore, P. A., Daniel T.C., Edwards D.R., Miller D.M., 1995. Effect of chemical  
13 amendments on ammonia volatilization from poultry litter. *J. Environ. Qual.* 24, 294-  
14 300.

15 Moset, V., Cambra-Lopez, M., Estelles, F., Torres, A.G., Cerisuelo, A., 2012. Evolution of  
16 chemical composition and gas emission from aged pig slurry during outdoor storage  
17 with and without prior solid separation. *Biosyst. Eng.* 3, 2-10.

18 Møller, H.B., Sommer, S.G., Ahring, B.K., 2002. Separation efficiency and particle size  
19 distribution in relation to manure type and storage conditions. *Bioresour. Technol.* 85  
20 (2), 189-196.

1 Resch, C., Braun, R. , Kirchmayr, R., 2008. The influence of energy crop substrates on  
2 the mass-flow analysis and the residual methane potential at a rural anaerobic  
3 digestion plant. *Water Sci. Technol.* 57, 73-81.

4 Parmar, K. A., Prajapati, S., Patel, R., Dabhi, Y., 2011. Effective use of ferrous and alum  
5 as a coagulant in treatment of dairy industry wastewater. *J. Eng. Appl. Sci.* 6, 42-45.

6 Perazzolo, F., Mattachini, G., Tambone, F., Misselbrook, T., Provolò, G., 2015. Effect of  
7 mechanical separation on emissions during storage of two anaerobically codigested  
8 animal slurries. *Agric. Ecosyst. Environ.* 207, 1-9.

9 Petersen, S.O., Andersen, A.J., Eriksen, J., 2012. Effects of cattle slurry acidification,  
10 ammonia and methane evolution during storage. *J. Environ. Qual.* 41, 88-94.

11 Petersen, S.O., Højberg, O., Poulsen, M., Schwab, C., and Eriksen, J., 2014.  
12 Methanogenic community changes, and emissions of methane and other gases, during  
13 storage of acidified and untreated pig slurry. *J. Appl. Microbiol.* 117(1), 160-172.

14 Popovic, O., Gioelli, F., Dinuccio, E., Balsari, P., 2014. Improved pig slurry mechanical  
15 separation using chitosan and biochar. *Biosyst. Eng.* 127, 115-124.

16 Sims, J.T. and Luka-McCafferty, N.J., 2002. On-farm evaluation of aluminum sulfate  
17 (Alum) as a poultry litter amendment: Effects on litter properties. *J. Environ. Qual.* 31,  
18 2066–2073.

19 Sommer, S.G., 1997. Ammonia volatilization from tanks containing anaerobically  
20 digested animal slurry. *Atmos. Environ.* 31, 863–868.

21 Stevens, R.J., Laughlin, R.J., Frost, J.P., 1989. Effect of acidification with sulfuric acid on  
22 the volatilization of ammonia from cow and pig slurries. *J. Agric. Sci.* 113, 389-395.

- 1 Vaddella, V.K., Ndegwa, P.M., Jeffrey, L.U., 2013. Mass transfer coefficients of  
2 ammonia for liquid dairy manure. *Atmos. Environ.* 66, 107-113.
- 3 Vandré, R., Clemens, J., 1997. Studies on the relationship between slurry pH,  
4 volatilization processes, and the influence of acidifying additives. *Nutr. Cycl.*  
5 *Agroecosys.* 47, 157–165.
- 6 Wang, K., Hung, D., Ying, H., Luo, H., 2014. Effects of acidification during storage on  
7 emissions of methane, ammonia, and hydrogen sulfide from digested pig slurry. *Biosys.*  
8 *Eng.* 122, 23-30.
- 9 Weiland, P., 2010. Biogas production, current state and perspectives. *Appl. Microbiol.*  
10 *Biotechnol.* 85, 849-860.
- 11 Weiske, A., Petersen, S.O., 2006. Mitigation of greenhouse gas emissions from  
12 livestock production. *Agric. Ecosyst. Environ.* 112, 105–106.

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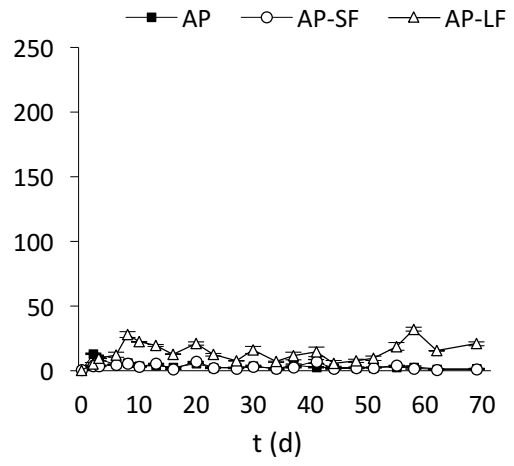
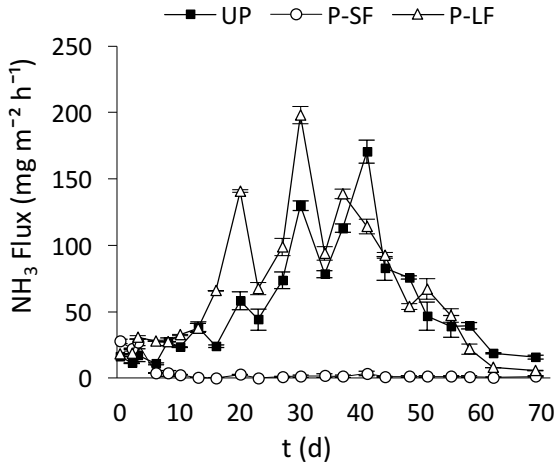
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1 **Fig. 1**

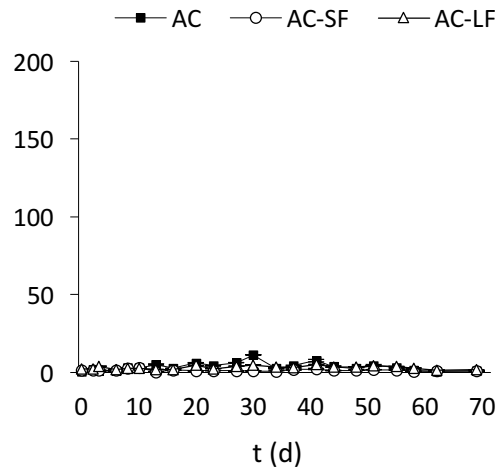
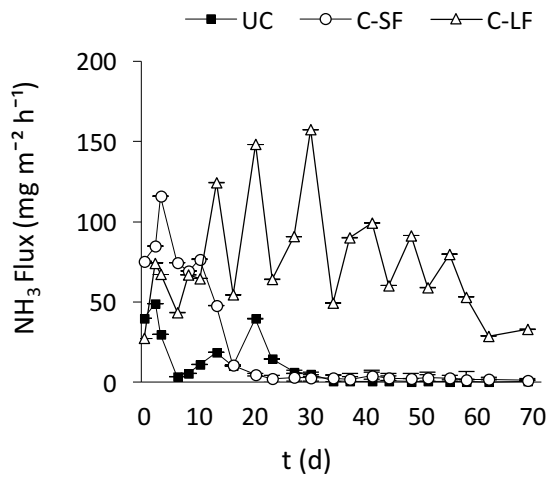
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**a) Raw pig slurry**



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**b) Co-digested pig slurry**



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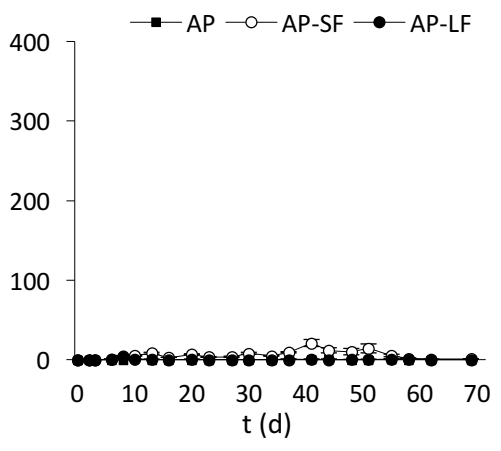
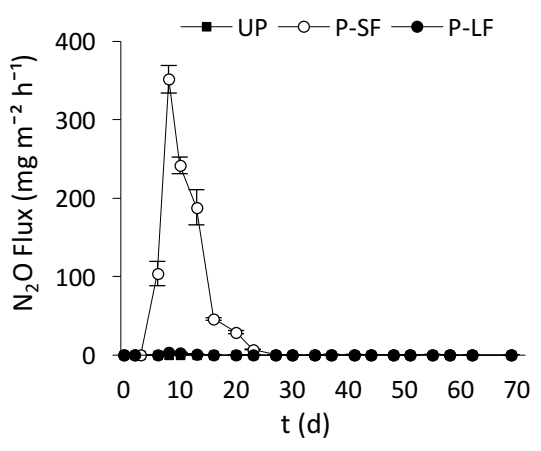
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1 **Fig. 2**

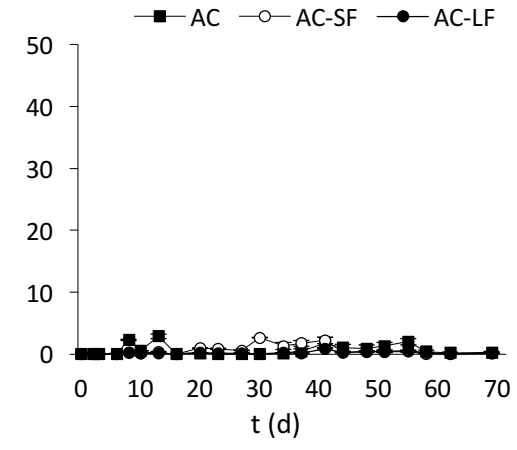
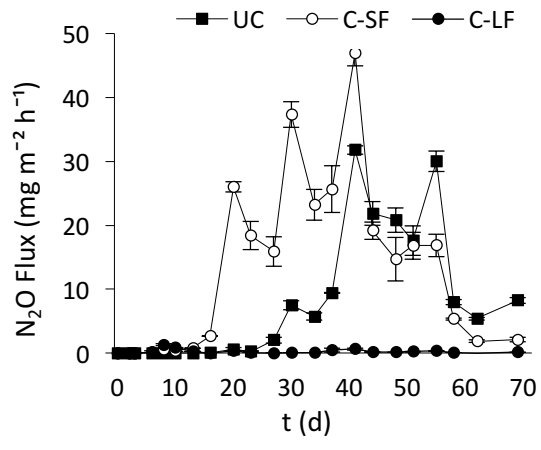
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**a) Raw pig slurry**



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**b) Co-digested pig slurry**



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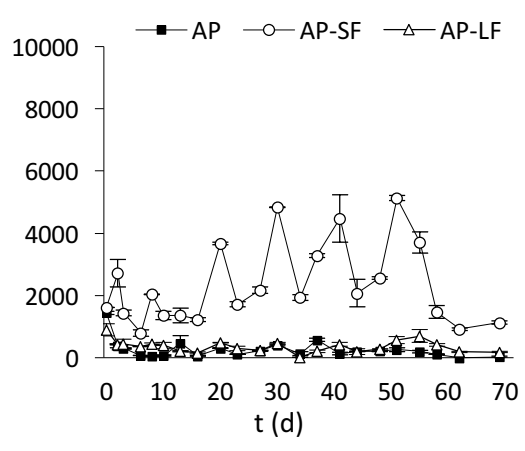
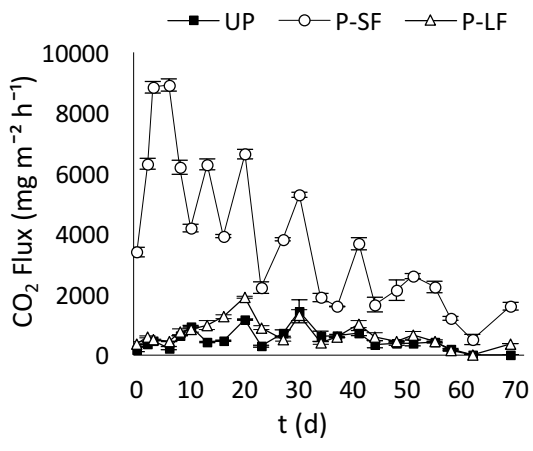
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1 **Fig. 3**

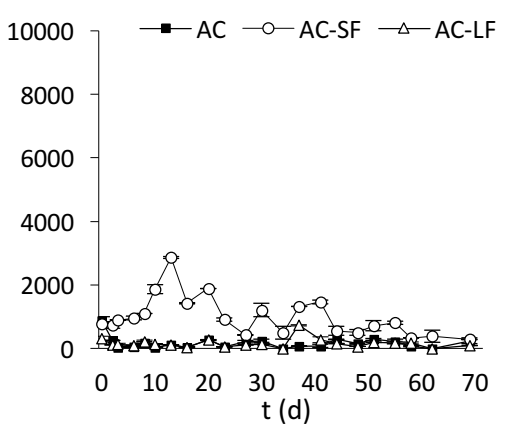
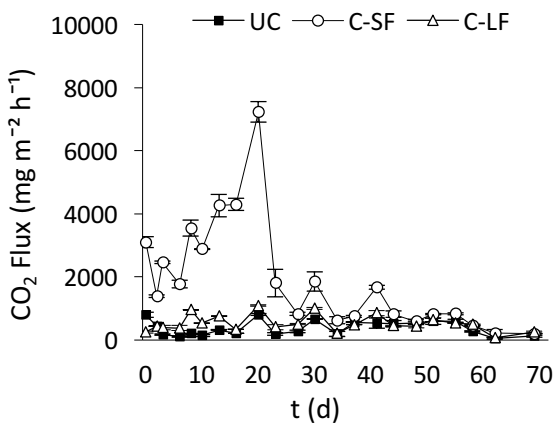
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**a) Raw pig slurry**



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**b) Co-digested pig slurry**



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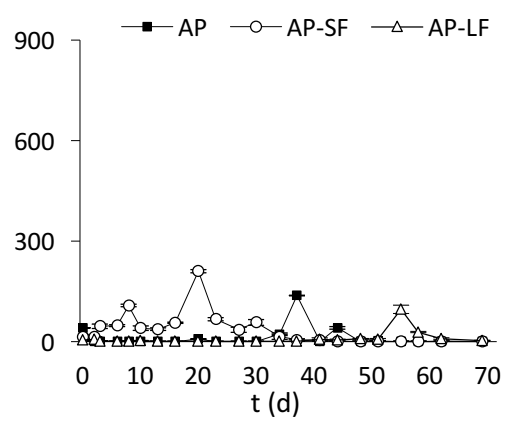
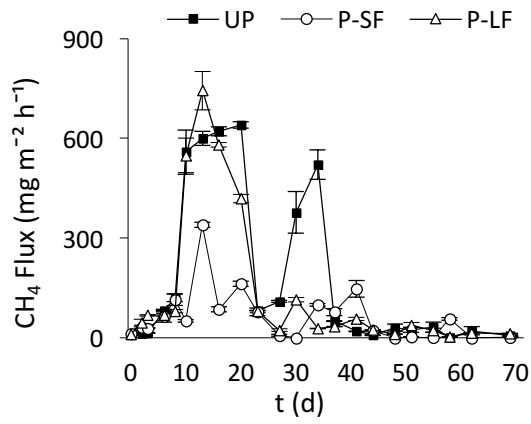
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1 **Fig. 4**

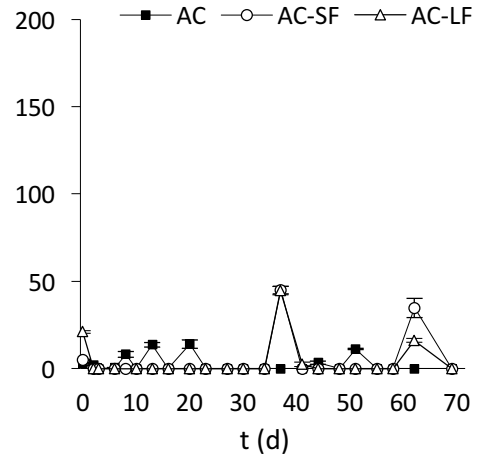
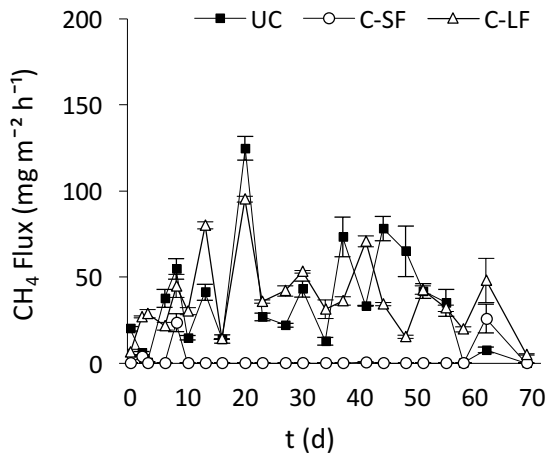
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**a) Raw pig slurry**



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**b) Co-digested pig slurry**



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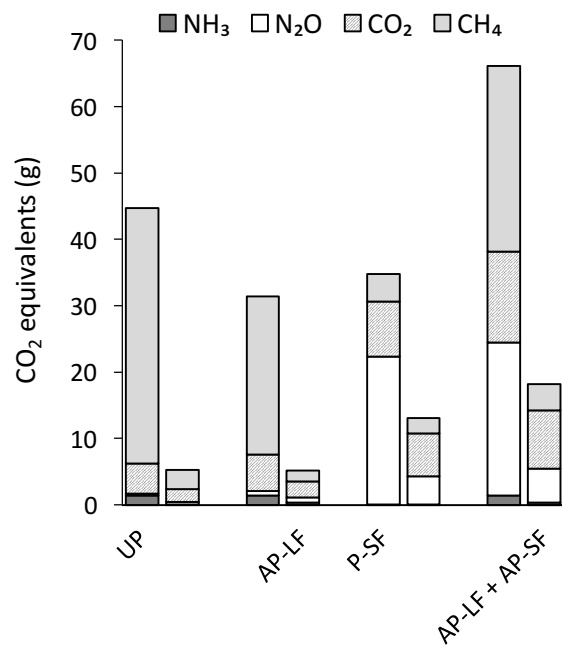
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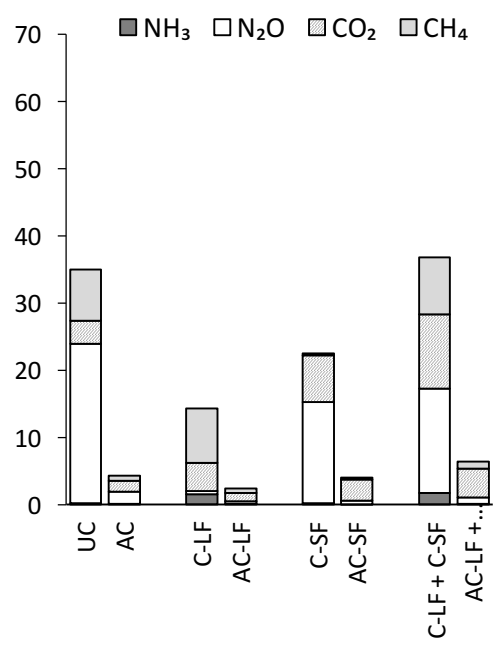
1 Fig. 5

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a) Raw pig slurry



b) Co-digested pig slurry



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1 **Table 1.** Main characteristics of untreated (non-acidified) and acidified raw and co-digested  
2 pig slurries at the beginning of the storage period, presented as mean values of three  
3 replicates with the standard deviations. For each parameter, means followed by different  
4 letters are significantly ( $P<0.05$ ) different from each other, based on a Tukey test.

Slurry type		pH	TS (g kg <sup>-1</sup> slurry)	VS (% of TS)	TN (g kg <sup>-1</sup> TS)	TAN (g kg <sup>-1</sup> TS)
<b>Raw pig slurry</b>	<b>UP</b>	7.28 (0.00) <sup>c</sup>	45.9 (0.75) <sup>i</sup>	77.8 (0.00) <sup>bc</sup>	53.7 (0.89) <sup>d</sup>	35.5 (0.65) <sup>d</sup>
	<b>P-LF</b>	7.44 (0.06) <sup>c</sup>	16.0 (0.95) <sup>k</sup>	62.2 (0.60) <sup>f</sup>	137.7 (3.98) <sup>a</sup>	101.7 (0.04) <sup>a</sup>
	<b>P-SF</b>	7.83 (0.12) <sup>b</sup>	160.6 (0.65) <sup>c</sup>	83.9 (1.80) <sup>a</sup>	24.9 (0.21) <sup>h</sup>	9.7 (0.10) <sup>i</sup>
	<b>AP</b>	5.50 (0.01) <sup>e</sup>	60.4 (0.55) <sup>g</sup>	69.7 (0.60) <sup>d</sup>	42.5 (0.47) <sup>f</sup>	31.3 (0.15) <sup>e</sup>
	<b>AP-LF</b>	5.53 (0.06) <sup>e</sup>	39.7 (0.25) <sup>j</sup>	58.5 (0.55) <sup>h</sup>	56.7 (0.28) <sup>cd</sup>	46.3 (0.65) <sup>b</sup>
	<b>AP-SF</b>	5.83 (0.06) <sup>d</sup>	135.5 (0.15) <sup>d</sup>	79.2 (0.10) <sup>b</sup>	23.00 (1.27) <sup>h</sup>	13.3 (0.45) <sup>g</sup>
<b>Co-digested pig slurry</b>	<b>UC</b>	7.85 (0.06) <sup>b</sup>	55.2 (0.24) <sup>h</sup>	67.6 (0.26) <sup>e</sup>	57.9 (0.66) <sup>c</sup>	40.1 (0.30) <sup>c</sup>
	<b>C-LF</b>	7.98 (0.00) <sup>b</sup>	42.5 (1.20) <sup>j</sup>	60.0 (0.05) <sup>g</sup>	73.1 (1.11) <sup>b</sup>	46.9 (0.65) <sup>b</sup>
	<b>C-SF</b>	8.36 (0.12) <sup>a</sup>	172.2 (0.55) <sup>a</sup>	84.8 (0.26) <sup>a</sup>	24.7 (0.97) <sup>h</sup>	11.4 (0.35) <sup>h</sup>
	<b>AC</b>	5.50 (0.01) <sup>e</sup>	85.8 (0.85) <sup>e</sup>	63.0 (0.45) <sup>f</sup>	31.8 (0.58) <sup>g</sup>	26.4 (0.40) <sup>f</sup>
	<b>AC-LF</b>	5.51 (0.01) <sup>e</sup>	71.4 (0.28) <sup>f</sup>	59.0 (0.25) <sup>h</sup>	48.8 (1.11) <sup>e</sup>	32.6 (0.70) <sup>e</sup>
	<b>AC-SF</b>	5.83 (0.06) <sup>d</sup>	163.0 (0.15) <sup>b</sup>	76.9 (0.05) <sup>c</sup>	26.5 (0.34) <sup>h</sup>	13.3 (0.20) <sup>g</sup>

5 **UP:** Untreated pig slurry, **LF:** Liquid fraction, **SF:** Solid fraction, **AP:** Acidified pig slurry,  
6 **UC:** Untreated co-digested pig slurry, **AC:** Acidified co-digested slurry, **TS:** Total solids,  
7 **VS:** Volatile solids, **TN:** Total nitrogen, **TAN:** Total ammonium nitrogen.

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**Table 2.** Cumulative emissions of ammonia (NH<sub>3</sub>), nitrous oxide (N<sub>2</sub>O), carbon dioxide (CO<sub>2</sub>), and methane (CH<sub>4</sub>) from untreated and acidified raw and co-digested pig slurries and their respective liquid and solid fractions during the 70 days of storage. Emissions of NH<sub>3</sub> are expressed as percentages of initial total nitrogen (TN) and total ammonium nitrogen (TAN) content, emissions of N<sub>2</sub>O are expressed as percentages of initial TN and emissions of C (CO<sub>2</sub> and CH<sub>4</sub>) are expressed as percentages of the initial volatile solids (VS) content. Values are presented as means of three replicates with standard errors. For each gas, means followed by different letters in each row are significantly (P<0.05) different from each other based on a Tukey test.

		Raw pig slurry		Co-digested pig slurry	
		UP	AP	UC	AC
N-NH <sub>3</sub> (% TN)	U	18.83 <sup>a</sup> (0.24)	1.04 <sup>c</sup> (0.06)	1.75 <sup>b</sup> (0.08)	1.39 <sup>bc</sup> (0.15)
	LF	25.66 <sup>a</sup> (0.76)	5.07 <sup>c</sup> (0.07)	18.45 <sup>b</sup> (0.16)	0.65 <sup>d</sup> (0.02)
	SF	0.99 <sup>b</sup> (0.06)	1.01 <sup>b</sup> (0.05)	9.80 <sup>a</sup> (0.57)	0.34 <sup>b</sup> (0.01)
N-NH <sub>3</sub> (% TAN)	U	31.92 <sup>a</sup> (0.40)	1.75 <sup>c</sup> (0.01)	2.96 <sup>b</sup> (0.08)	1.84 <sup>c</sup> (0.13)
	LF	39.20 <sup>a</sup> (0.20)	7.53 <sup>c</sup> (0.06)	30.77 <sup>b</sup> (0.20)	1.26 <sup>d</sup> (0.08)
	SF	2.00 <sup>b</sup> (0.32)	2.47 <sup>b</sup> (0.02)	26.60 <sup>a</sup> (0.14)	0.84 <sup>c</sup> (0.03)
N-N <sub>2</sub> O (% TN)	U	0.03 <sup>b</sup> (0.00)	0.04 <sup>b</sup> (0.00)	1.64 <sup>a</sup> (0.07)	0.12 <sup>b</sup> (0.01)
	LF	0.12 <sup>a</sup> (0.01)	0.08 <sup>ab</sup> (0.00)	0.05 <sup>bc</sup> (0.01)	0.04 <sup>c</sup> (0.00)
	SF	9.20 <sup>a</sup> (0.23)	1.89 <sup>c</sup> (0.01)	6.55 <sup>b</sup> (0.22)	0.16 <sup>d</sup> (0.01)
C-CO <sub>2</sub> (% VS)	U	7.42 <sup>a</sup> (0.23)	2.07 <sup>c</sup> (0.08)	4.20 <sup>b</sup> (0.31)	1.39 <sup>c</sup> (0.07)
	LF	24.30 <sup>a</sup> (0.08)	6.20 <sup>c</sup> (0.44)	9.69 <sup>b</sup> (0.21)	1.77 <sup>d</sup> (0.03)
	SF	19.28 <sup>a</sup> (0.26)	14.11 <sup>c</sup> (0.07)	17.23 <sup>b</sup> (0.11)	6.18 <sup>d</sup> (0.06)
C-CH <sub>4</sub> (% VS)	U	5.83 <sup>a</sup> (0.28)	0.32 <sup>bc</sup> (0.01)	0.87 <sup>b</sup> (0.01)	0.07 <sup>c</sup> (0.01)
	LF	13.24 <sup>a</sup> (0.16)	0.43 <sup>c</sup> (0.03)	1.94 <sup>b</sup> (0.06)	0.10 <sup>c</sup> (0.00)
	SF	0.95 <sup>a</sup> (0.02)	0.49 <sup>b</sup> (0.00)	0.07 <sup>c</sup> (0.00)	0.08 <sup>c</sup> (0.00)

1 **U**: Unseparated slurry, **LF**: Liquid fraction, **SF**: Solid fraction, **UP**: Untreated pig slurry,  
2 **AP**: Acidified pig slurry, **UC**: Untreated co-digested slurry, **AC**: Acidified co-digested  
3 slurry.

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1 **Table 3.** Main characteristics of untreated (non-acidified) and acidified raw and co-digested pig slurries at  
2 the end of the storage period, presented as mean values of three replicates with the standard deviations.  
3 For each parameter, means followed by different letters are significantly ( $P < 0.05$ ) different from each  
4 other, based on a Tukey test.

Slurry type		pH	TS (g kg <sup>-1</sup> )	VS (% of TS)	TN (g kg <sup>-1</sup> TS)	TAN (g kg <sup>-1</sup> TS)	Slurry loss (kg)
<b>Raw pig slurry</b>	<b>UP</b>	8.24 (0.11) <sup>b</sup>	43.1 (0.45) <sup>h</sup>	69.6 (0.05) <sup>bc</sup>	25.7 (2.82) <sup>fg</sup>	5.9 (0.20) <sup>g</sup>	1.2 (0.10) <sup>bc</sup>
	<b>P-LF</b>	8.57 (0.06) <sup>a</sup>	18.7 (3.95) <sup>i</sup>	51.2 (3.02) <sup>g</sup>	34.4 (0.70) <sup>de</sup>	4.7 (0.25) <sup>h</sup>	1.4 (0.10) <sup>a</sup>
	<b>P-SF</b>	7.21 (0.04) <sup>de</sup>	182.5 (1.47) <sup>c</sup>	72.6 (1.55) <sup>b</sup>	18.2 (0.45) <sup>i</sup>	0.5 (0.05) <sup>i</sup>	0.9 (0.05) <sup>d</sup>
	<b>AP</b>	6.75 (0.04) <sup>f</sup>	78.2 (0.56) <sup>f</sup>	65.91 (0.05) <sup>cd</sup>	30.3 (1.30) <sup>ef</sup>	25.5 (0.35) <sup>c</sup>	1.1 (0.05) <sup>c</sup>
	<b>AP-LF</b>	7.00 (0.19) <sup>ef</sup>	54.6 (0.20) <sup>g</sup>	57.1 (1.15) <sup>ef</sup>	42.8 (1.61) <sup>a</sup>	34.1 (0.05) <sup>a</sup>	1.3 (0.05) <sup>ab</sup>
	<b>AP-SF</b>	5.33 (0.17) <sup>i</sup>	186.6 (2.06) <sup>c</sup>	64.8 (1.05) <sup>d</sup>	23.6 (1.44) <sup>gh</sup>	6.3 (0.17) <sup>g</sup>	1.1 (0.05) <sup>c</sup>
<b>Co-digested pig slurry</b>	<b>UC</b>	7.73 (0.01) <sup>c</sup>	64.9 (0.69) <sup>g</sup>	62.1 (0.80) <sup>d</sup>	37.3 (2.15) <sup>bcd</sup>	24.3 (0.00) <sup>d</sup>	1.1 (0.05) <sup>c</sup>
	<b>C-LF</b>	8.36 (0.05) <sup>ab</sup>	43.8 (0.19) <sup>h</sup>	50.8 (3.10) <sup>g</sup>	39.4 (2.15) <sup>abc</sup>	9.16 (0.55) <sup>f</sup>	1.2 (0.10) <sup>bc</sup>
	<b>C-SF</b>	7.34 (0.17) <sup>d</sup>	240.6 (11.15) <sup>b</sup>	77.7 (1.95) <sup>a</sup>	19.4 (0.81) <sup>hi</sup>	1.13 (0.05) <sup>i</sup>	0.5 (0.00) <sup>e</sup>
	<b>AC</b>	6.35 (0.06) <sup>g</sup>	118.3 (0.55) <sup>d</sup>	61.1 (0.55) <sup>de</sup>	34.9 (0.15) <sup>cde</sup>	24.2 (0.36) <sup>d</sup>	1.0 (0.05) <sup>cd</sup>
	<b>AC-LF</b>	5.85 (0.02) <sup>h</sup>	100.2 (0.95) <sup>e</sup>	52.7 (0.65) <sup>fg</sup>	40.0 (1.21) <sup>ab</sup>	31.6 (0.70) <sup>b</sup>	1.2 (0.00) <sup>bc</sup>
	<b>AC-SF</b>	5.82 (0.05) <sup>h</sup>	269.1 (2.22) <sup>a</sup>	61.6 (0.45) <sup>de</sup>	30.5 (2.25) <sup>e</sup>	15.5 (0.30) <sup>e</sup>	0.9 (0.05) <sup>d</sup>

5 **UP:** Untreated pig slurry, **LF:** Liquid fraction, **SF:** Solid fraction, **AP:** Acidified pig slurry, **UC:** Untreated co-digested  
6 pig slurry, **AC:** Acidified co-digested slurry, **TS:** Total solids, **VS:** Volatile solids, **TN:** Total nitrogen, **TAN:** Total  
7 ammonium nitrogen.

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