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Title page

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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Highlights

- Acidification and separation of slurries were combined to reduce gaseous emissions
- Acidification reduced ammonia emissions during mechanical separation.
- Acidification reduces NH_3 and GHG emissions during storage of slurries
- Total GHGs from acidified fractions were lower than from non-acidified fractions.

Abstract

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

The aim of this study was to assess the effects of acidification before the separation of raw and co-digested pig slurries on the gaseous emissions during the storage of the resulting liquid fraction (LF) and SF. The emission rates of NH_3, N_2O, CO_2, and CH_4 were followed during 70 days of storage.

Acidification applied before separation significantly reduced the emissions of NH_3 and GHG during the storage of the fractions from raw and co-digested slurries. The main reductions were observed in the acidified fractions, relative to the non-acidified fractions (that led to the highest gaseous emissions), in both slurries. Thus, NH_3 and CH_4 emissions were significantly reduced in acidified LFs and N_2O emissions were significantly reduced in acidified SFs. The CO_2 emissions were significantly reduced in both acidified fractions from both slurries, since most of the inorganic C was released during the acidification process.

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

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

1. Introduction

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

Emissions of ammonia (NH_3) and greenhouse gases (GHG) such as nitrous oxide (N_2O), methane (CH_4), and carbon dioxide (CO_2), the main gases emitted from slurries (Weiske and Petersen, 2006), affect the health of humans and other animals and damage the environment (Erisman et al., 2008). Therefore, finding a proper way to reduce these emissions has become an important issue (CEC, 2005).

Over the past few years anaerobic co-digestion of organic substrates (such as energy crops and agro-industrial byproducts) and livestock manures has become increasingly popular in Europe. However, the output from digesters (co-digested slurry) still contains high amounts of organic matter which has not been completely degraded, leading to residual GHG emissions (Dai et al., 2013). Co-digested slurry contains also large amounts of ammonium (NH_4^+); thus, NH_3 emissions also occur during storage (Sommer, 1997; Resch et al., 2008).

Acidification of slurries is a treatment known to reduce NH_3 emissions (Stevens et al., 1989; Kai et al., 2008; Fangueiro et al., 2015) and recent studies have demonstrated its capacity to reduce CH_4 emissions as well (Ottosen et al., 2009; Petersen et al., 2012; Wang et al., 2014). Currently, concentrated sulfuric acid is used as an acidification additive in Denmark (Eriksen et al., 2008). However, there are some concerns related to the use of this strong acid (Borst, 2001). Several studies have shown disadvantages related to its use, including excess foam formation (increasing the storage capacity required) and the pool of excess sulfur created - which can lead to significant hydrogen sulfide (H_2S) emissions (Vandré and Clemens, 1997; Dai et al., 2013). Aluminum sulfate ($Al_2(SO_4)_3$), referred to hereafter as alum, is an acidifying additive which has been used successfully to reduce NH_3 volatilization in poultry litter (Moore et al., 1995; Sims and Luka-McCafferty, 2002). Alum is also known for its flocculant properties in wastewater treatment (Parmar et al., 2011), which suggests that it may positively affect the mechanical separation of slurry. Therefore, alum was used here as an acidifying additive to decrease the pH of raw and co-digested pig slurries.

Mechanical separation is currently applied in some European countries and has been widely used in Asia (Hjorth et al., 2010). It provides a liquid fraction (LF), rich in soluble N, that can be used directly on-farm as a N fertilizer, and a solid fraction (SF), rich in total solids (TS), organic matter (OM), and phosphorus, which is normally transported to other farming areas where nutrients and OM are needed (Hjorth et al., 2010). Nevertheless, previous studies (Dinuccio et al., 2008; Fangueiro et al., 2008) have demonstrated that the total amount of gaseous emissions from the separated fractions is higher than from the non-separated slurries. A recent study by Perazzolo et al. (2015) showed similar results in terms of gaseous emissions from fractions of co-digested slurry, and suggested the adoption of mitigation techniques for the management of separated co-digestates. Some studies have assessed the effects of acidification of pig slurry (Dai and Blanes-Vidal, 2013; Petersen et al., 2012) and digested slurry (Wang et al., 2014) on gaseous emissions during storage, but there is no study reporting the effects on gaseous emissions during storage of the fractions obtained from acidified and separated raw and co-digested slurries.

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

The aim of this study was to assess the effects of the combined acidification and separation of raw and co-digested pig slurry on NH_3, CO_2, CH_4, and N_2O emissions during 70 days of storage.

2. Material and methods

2.1 Slurry treatment

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

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

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

2.2 Storage conditions

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

2.3 Slurry analysis

All the materials tested were analyzed at the beginning and end of the storage period for their pH, total solids (TS), volatile solids (VS), total nitrogen (TN), and total ammonium (NH_4^+) content. The TN content was analyzed by the Kjeldahl method (Horneck & Miller, 1998). The TS content was determined after drying 10 g of fresh material at 105°C to constant weight for 24 hours and the VS content by loss on ignition after calcination at 550°C for 3 hours (Clesceri et al., 1989). The total NH_4^+ content was analyzed after extraction with 30 mL of 0.05 M $CaCl_2$ (van Raij, 1998; Houba et al., 2000), by segmented flow colorimetry (Skalar ScanPlus, The Netherlands). The main characteristics of the slurries at the beginning and end of the storage period are given in Tables 1 and 3.

2.4 Gas measurements and calculations

The losses of NH_3, CO_2, CH_4, and N_2O were measured by the dynamic chamber method described in Berg et al. (2006).

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

The outlet port was connected by a Teflon tube to an infrared photoacoustic analyzer (1412 Multi-gas Monitor, Innova® Air Tech Instruments, Ballerup, Denmark) for gas concentration measurements. The instrument was calibrated before the beginning of the experiment by the manufacturer and was run with corrections for cross interferences between water vapor, CO_2, and N_2O and cross compensation (Dinuccio et al., 2008). The gas concentrations at the outlet were recorded for 16 minutes, to have eight measurements for each slurry sample. Of these eight values, the first three were rejected in order to have a representative measurement: the mean of the last five values recorded.

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

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

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

The reduction efficiencies R (%) of the NH_3, CO_2, CH_4, and N_2O emissions from acidified slurries and their fractions, relative to untreated slurries (Wang et al., 2014), were calculated as follows (Eq. 2):

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

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

$$Relative\ emission\ (\%) = \frac{F_{Acidified\ slurry}}{F_{Untreated\ slurry}}\, x\ 100 \qquad \text{(Eq. 3)}$$

The cumulative emissions (mg vessel^{-1}) for each gas during the whole storage period were calculated by the mean values between two sampling events multiplied by the time interval between them, as described in Fangueiro et al. (2008). The cumulative carbon (CH_4 and CO_2) and nitrogen (NH_3 and N_2O) emissions were expressed as percentages (%) of the respective initial volatile solids (VS) and total nitrogen (TN) content in each slurry and fraction.

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

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

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

To assess the global warming potential (GWP) of each treatment, the N_2O and CH_4 cumulative emissions were converted to CO_2 equivalents by using their respective GWPs. According to IPCC (2013), in a 100-year time horizon, the GWP values are 298 and 25 for N_2O and CH_4, respectively. For NH_3 emissions, the value is estimated to be 1% of the deposited N_2O (de Vries et al., 2011).

2.5 Statistical analysis

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

3. Results and discussion

3.1 Initial slurry characteristics

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

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

The total nitrogen (TN) content was significantly ($P<0.05$) higher in UC (57.9 g kg^{-1} TS) than in UP (53.7 g kg^{-1} TS) and in both cases was not affected by acidification. The TN concentration was significantly ($P<0.05$) decreased by acidification (on a dry weight basis). However, the reduction in TN concentration was mainly due to the increase in the TS content and was not significant when considering the concentration on a wet weight basis (Table 1).

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

3.2 Gaseous emissions during storage

3.2.1 NH_3 emissions

For the raw pig slurry, ammonia (NH_3) emissions occurred mainly from the untreated slurry (UP) and from its derived LF, and both followed the same trend (Fig. 1a). The emissions started to rise from the beginning of the storage - to reach a peak of 170 mg NH_3 m^{-2} h^{-1} at day 41 for UP and of 198 mg NH_3 m^{-2} h^{-1} at day 30 for the P-LF, slightly decreasing afterwards until the end of the storage (Fig. 1a). These NH_3 emissions accounted for losses of 18.8% (UP) and 25.7% (P-LF) of the initial N content and losses of 31.9% (UP) and 39.2% (P-LF) of the initial TAN content (Table 2).

Untreated co-digested slurry (UC) and its fractions followed a different trend - relative to raw slurry - regarding NH_3 emissions, with C-LF and C-SF showing the highest emissions (Fig. 1b). The C-LF showed a gradual increase during the first 2 weeks, reaching a peak (157 mg NH_3 m^{-2} h^{-1}) at day 30 before slightly decreasing until the end of the storage. In contrast, the emissions from UC and C-SF were highest during the first week and showed a gradual decrease from the beginning of the storage, reaching undetectable values after 4 and 3 weeks, respectively. The UC showed values that were always under 50 mg NH_3 m^{-2} h^{-1} and C-SF had the highest peak (116 mg NH_3 m^{-2} h^{-1}) at day 3 (Fig. 1b), decreasing drastically afterwards. The highest NH_3 emissions observed from C-LF and C-SF accounted for a total N loss of 18.5% and 9.8% of the initial N content and a total loss of 30.8% and 26.6% of the initial TAN content, respectively (Table 2).

The main differences observed regarding NH_3 emissions between raw and co-digested slurry can be attributed to the initial slurry characteristics (Table 1). Besides the chemical composition, the co-digested slurry originated from an anaerobic digester fed with 67% pig slurry, 23% maize and triticale silage, and 10% farmyard manure and cattle slurry. Undigested silage may explain the higher content of large particles in the co-digested slurry, in comparison with the raw slurry. These particles normally have a high content of cellulose and lignin; therefore, there may have been less C readily available for degradation than in the raw slurry and thus, less mineral N should be immobilized by microorganisms. To verify this statement, VS losses during storage were calculated by mass balances using the initial and final analyses of the slurries (Tables 1 and 3). The decrease in the VS content was greater in raw (41%) than in co-digested slurry (22%), confirming that the catabolic activity was higher in the raw pig slurry. The decarboxylation of organic acids consumes protons and raises the pH, with the corresponding release of NH_3 (Petersen et al., 2012). The raw slurry, after the 70-d storage, had undergone a greater increase in pH than the co-digested slurry (Table 3) - another indicator giving support to previous findings.

Previous studies showed that the initial slurry characteristics affect the separation performance of the slurry (Møller et al., 2002). Thus, the differences observed in the NH_3 volatilization of the LFs and SFs from both slurries can be attributed to the initial composition of the fractions. As explained before, the co-digested slurry had larger particles, which were transferred to the SF. The P-SF was more compacted than the C-SF and thus had a higher density (563 kg m^{-3}) than the C-SF (300 kg m^{-3}). The lower density of the C-SF may be related to the high content of straw in the co-digestate, which was transferred to the SF. Straw normally contains high amounts of lignin and cellulose, which are not readily degradable by microorganisms (Hansen et al., 2006). Thus, microbial activity should be lower and immobilization of ammonium may be minimal, allowing NH_3 release.

Acidification of slurries reduced NH_3 emissions drastically during the whole storage period, with values always below 33 and 11 mg NH_3 m^{-2} h^{-1} in acidified raw pig slurry (AP) and co-digested slurry (AC), respectively (Fig. 1).

The mean NH_3 reduction efficiencies obtained by acidifying raw and co-digested slurries were 92% and 70%, respectively, relative to the non-acidified slurries. The acidified fractions from raw slurry, AP-LF and AP-SF, showed reductions of 78% and 31%, respectively, while 96% reductions were observed for both fractions of the acidified co-digested slurry, AC-LF and AC-SF.

The reductions in NH_3 emissions obtained in our study were greater than those of previous studies where sulfuric acid was used as the acidifying additive. Dai and Blanes-Vidal (2013) obtained a reduction of 77% when lowering the pH of pig slurry to 5.5 and Wang et al. (2014) observed a daily mean reduction of 40.2% for acidified digested slurry. These differences may be partially due to the initial higher TS content of the acidified slurries in our study (Vaddella et al., 2013). According to De Visscher et al. 2002 the adsorption of N-NH_4^+ on suspended organic solids reduces the diffusion coefficient resulting in lower NH_3 volatilization. In addition, at the end of the storage period in our study, the acidified slurries had pH values lower than the initial pH of the non-acidified slurries (and lower than the values in previous studies), meaning that a low and stable pH was maintained in the acidified slurries during storage. This was probably due to the use of alum, which - in contrast to sulfuric acid - should not be buffered so fast and therefore CO_2 emissions and the consequent NH_3 release should be lower. The NH_3 emissions from acidified slurries in our study showed a slight increase after week 2, while the acidified slurries in Dai and Blanes-Vidal (2013) and in Wang et al. (2014) had a faster and higher increase in NH_3 emissions; these differences explain, as well, the higher reduction efficiencies obtained in our study.

Previous studies by Dinuccio et al. (2008) and Fangueiro et al. (2008) have shown NH_3 emissions to increase when raw slurry is separated. The same findings were observed by Perazzolo et al. (2015) when separating co-digested slurry. This increase was mainly due to high NH_3 volatilization from the LF. Vaddella et al. (2013) demonstrated a higher degree of NH_3 volatilization when the TS content decreased. When acidification was applied in our study, a higher TS content was obtained in the LFs and, thus, NH_3 volatilization was lower. Therefore, the NH_3 emissions from the separated fractions together were less than from untreated slurries.

3.2.2 N_2O emissions

Nitrous oxide (N_2O) emissions are a byproduct of the nitrification/denitrification process which occurs when both aerobic and anaerobic conditions coexist in manure (Loyon et al., 2007). According to the measured N_2O emissions, such conditions only appeared in the SFs from both slurries and in the untreated co-digested (UC) slurry. In the remaining samples, N_2O emissions during the 70-day storage period were minimal, as the conditions were mainly anaerobic (Fig. 2). Emissions of N_2O from the P-SF occurred between days 6 and 23 of the storage, reaching a peak (351 mg N_2O m^{-2} h^{-1}) at day 8 (Fig. 2a). These results are in agreement with previous studies by Dinuccio et al. (2008) and can be attributed to the aerobic conditions and lower moisture content of the SFs.

The C-SF showed lower N_2O emission rates than P-SF, reaching a peak at day 41 (47 mg N_2O m^{-2} h^{-1}). At day 16 the emission started to decrease, until the end of the storage. Untreated co-digested slurry had a high content of straw, which was displaced towards the surface of the vessel during the storage due to its lower density in relation to the liquid. This straw dried out with time due to water evaporation and acted as a surface crust, with some aerobic zones in between the anaerobic parts. Therefore, the nitrification/denitrification process, and thus the N_2O release, may have taken place here. In agreement with our results, previous studies (Sommer et al., 2000; Berg et al., 2006) found N_2O production only when a dry crust was present on the slurry. In our study this crust became drier with time - which may explain why the N_2O emissions started at day 27 in UC. The N_2O emission reached its peak at day 41 (32 mg N_2O m^{-2} h^{-1}), decreasing afterwards until the end of storage (Fig. 2b).

The decrease of the TAN content during storage was greater than that of the TN content in P-SF, C-SF, and UC, indicating that some NH_4^+ may have been nitrified during storage - leading to N_2O release. It is of note that the NH_3 emissions decreased as the proportion of oxidized NH_4^+ increased. The emission of NH_3 dropped when the N_2O emission started to rise: at days 6 and 20 in P-SF and C-SF, respectively, and at day 27 in UC.

The cumulative emission of N_2O accounted for a loss of 9.2% and 6.6% of the initial total N content in P-SF and C-SF, respectively (Table 2). Dinuccio at al. (2008) observed a lower N_2O emission rate in the SF from pig slurry and a corresponding lower percentage loss of N. This may have been due to a higher density of the SF in our study, which limits NH_3 emission and increases the proportion of the NH_4^+ content undergoing nitrification (Hansen et al., 2006). The N_2O emissions from UC accounted for a loss of 1.6% of the initial N content (Table 2). The N_2O emission rate from C-SF was much lower than in P-SF; so, the high percentage loss of N from C-SF was due to the lower initial N content, as this fraction had a lower density than P-SF (Table 1).

Acidification inhibited N_2O emissions, during the whole storage period, from the SFs of both slurries and untreated co-digested slurry (Fig. 2). Acidification may have inhibited the nitrification/denitrification process, as N_2O emissions were significantly reduced and nitrate was not detected in acidified slurries at the end of the storage. Accordingly, previous studies reported a delay/decrease of nitrification in acidified slurry following soil application (Fangueiro et al., 2013). The mean reduction efficiencies for N_2O were 91% and 95% for UC and C-SF, respectively, and 88% for P-SF.

3.2.3 CO_2 emissions

The emission rates of carbon dioxide (CO_2) showed high variability during the whole storage period, with the highest rates observed in the first three weeks of storage (Fig. 3). Significantly higher emissions of CO_2 were observed from P-SF and C-SF, which peaked at days 6 (8921 mg CO_2 m^{-2} h^{-1}) and 20 (7232 mg CO_2 m^{-2} h^{-1}), respectively, before decreasing to values lower than 2000 mg CO_2 m^{-2} h^{-1} at day 30. The cumulative CO_2 emissions from the SFs accounted for a total C loss (present in the initial VS content) of 19.3% and 17.2% of the initial C content in P-SF and C-SF, respectively (Table 2).

The CO_2 emissions are related to the amount of C present in the slurries (Fangueiro et al., 2008); thus, fractions with a higher C content have higher CO_2 emission rates. In accordance with this, the SFs in our study which had a higher C content (Table 1) were the ones showing higher CO_2 emissions. In addition, SFs have greater aeration relative to untreated slurries and LFs, which results in higher aerobic microbial activity.

The two main sources of CO_2 emission are the microbial degradation of organic matter and urea mineralization (Moset et al., 2012). The high CO_2 release from C-SF during the first three weeks of storage could have been due to these two processes, but also to a higher rate of organic N mineralization. This organic N transformation is accompanied by NH_3 volatilization which, as shown before (Fig. 1b), was significant during the first three weeks. The CO_2 emissions dropped after 30 days in the SFs from both slurries, probably due to depletion of the easily degradable C. In addition, the reduction of slurry volume due to water evaporation and sample compaction diminishes the aerobic nature of the conditions, which consequently reduces the microorganism-mediated aerobic degradation.

Acidification significantly ($P<0.05$) reduced the CO_2 emissions from both slurries and fractions, except from day 30 onwards - when acidified SFs showed higher CO_2 values than non-acidified SFs (Fig. 3). The mean reduction efficiencies for CO_2 were 48% and 54% for AP and AC, respectively, 48% and 70% for AP-LF and AC-LF, respectively, and 41% and 46% for AP-SF and AC-SF, respectively. Most of the dissolved CO_2 is lost during the acidification process (Fangueiro et al., 2008); therefore, the high reduction in CO_2 emissions during the storage of acidified slurries was partly due to this process. However, the maintenance of low CO_2 emissions during storage also affects the NH_3 volatilization - which, as shown before, was significantly reduced during the storage of acidified slurries.

3.2.4 CH_4 emissions

Methane (CH_4) is released from slurry as a consequence of C degradation in anaerobic conditions (Hansen et al., 2006). Methane emissions were mainly observed in the untreated slurries and LFs from both slurries, with higher rates in raw than in co-digested pig slurry (Fig. 4). This, as explained before, was due to the higher level of readily degradable C present in raw slurry, relative to co-digested slurry, as most of the easily degradable matter in co-digested slurry had been lost during the anaerobic digestion (Perazzolo et al., 2015).

Methane emissions from UP started to rise from the beginning of the storage, reaching peaks at days 20 (641 mg CH_4 m^{-2} h^{-1}) and 34 (522 mg CH_4 m^{-2} h^{-1}) before decreasing to values < 50 mg CH_4 m^{-2} h^{-1} from day 37 (Fig. 4a). The P-LF and P-SF followed the same trend, with a peak of 743 mg CH_4 m^{-2} h^{-1} for P-LF and of 340 mg CH_4 m^{-2} h^{-1} for P-SF, in both cases on day 13 (Fig. 4a). These CH_4 emissions accounted for a loss (as a % of the C present in the initial VS content) of 5.8%, 13.2%, and 1% of the initial C content in UP, P-LF, and P-SF, respectively (Table 2). This C loss as CH_4 is in accordance with the values observed by Dinuccio et al. (2008) for pig slurry stored at 25°C, this temperature being the mean temperature also registered in our study over the whole storage period.

The CH_4 emissions from UC and C-LF showed high variability during storage, following the same trend as raw pig slurry, and the values for C-SF were negligible (Fig 4b). A slight increase in the CH_4 emissions from UC and C-LF was observed at the beginning of storage, reaching a peak at day 20 in both UC (125 mg CH_4 m^{-2} h^{-1}) and C-LF (95 mg CH_4 m^{-2} h^{-1}) and slightly decreasing afterwards until the end of the storage (Fig. 4b). The cumulative CH_4 emissions in both cases accounted for less than 2% of the total initial C content (Table 2).

Acidification may alter methanogenic activity, as the process is normally inhibited at pH values below 6 (Weiland, 2010). Acidification reduced the CH_4 emissions from both slurries and fractions (Fig. 4), with mean reduction efficiencies of 81% and 92% for AP and AP-LF, respectively. The mean CH_4 emissions were reduced in AC and AC-LF, by 91% in both cases. Wang et al. (2014) observed a mean CH_4 reduction efficiency of 80.8% when acidifying digested pig slurry to pH 5.5. This small difference in reduction efficiencies could be due to the different timeframe in the calculation by Wang et al. (2014), as they only considered the first 20 days of storage while we considered the whole period (70 days). However, our reduction efficiencies closely resemble the values observed by Petersen et al. (2014), who found that CH_4 emissions were reduced by 94% when pig slurry was acidified during storage.

3.3 Effect of the combined acidification and separation on GHG emissions

To assess the effects of acidification applied before separation on net total GHG emissions, the global warming potential (GWP) for each gas was considered in order to express an overall effect in terms of CO_2 equivalents (Fig. 5).

Separation alone significantly increased the net total GHG emissions of the solid and liquid fractions (combined together): by 48% for raw slurry and by 5% for co-digested slurry, relative to the untreated slurries (Fig. 5). The increment observed when raw pig slurry was separated was mainly due to the increase in N_2O emissions from SF, the increase in CH_4 emissions from LF, and the increase in CO_2 emissions from both LF and SF (Fig. 5). This is in accordance with previous results obtained by Dinuccio et al. (2008), where the combined emissions from separated fractions were always higher than from unseparated slurries. However, when acidification was applied before separation, the net total GHG emissions of the acidified fractions combined together were significantly lower than from untreated slurries.

Reductions in the net total GHG emissions of 59% and 81% were observed for the sum of the acidified fractions from raw and co-digested slurry, respectively, relative to untreated slurries. The reductions for acidified raw slurry were mainly due to the lower CH_4 loss from the acidified LF and to the lower loss of N_2O from the acidified SF, relative to the corresponding non-acidified fractions. The decrease for co-digested slurry was mainly due to the undetectable values of N_2O and CH_4 for acidified SF and LF, respectively, and to the smaller loss of CO_2 from both acidified fractions, relative to the corresponding non-acidified fractions (Fig. 5).

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

3.4 Final slurry characteristics

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

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

After storage, the TN and TAN concentrations of the pig and co-digested slurries had significantly decreased, with PS and CS and their respective LFs showing the highest N losses (Table 3). The N losses were 68% and 40% in the PS and CS slurry, respectively, which are mainly attributable to NH_3 volatilization as the TAN values were reduced by 88% and 50%, respectively.

The same trend was followed by the LFs from both slurries, with TN losses of 77% and 65% from P-LF and C-LF, respectively. These fractions showed an almost complete loss of TAN: 95% and 86% in P-LF and C-LF, respectively. These results are in agreement with the studies by Perazzolo et al. (2015) and Fangueiro et al. (2008), where the losses were highest in the LFs because they had the highest TAN:TN ratios and low TS contents.

The N losses from the SFs may have been due partially to NH_3 volatilization but also to some immobilization and/or nitrification of the TAN. The TN in the SFs declined by 43% and 35% and the TAN by 96% and 92% in P-SF and C-SF, respectively. Some immobilization may have occurred in these SFs, promoted by their high C:N ratios. On the other hand, nitrate (NO_3^-) was detected in the C-SF at the end of the storage, confirming that some nitrification may have occurred as well. Nitrification is known to occur in the SF as the oxygenation is allowed so aerobic conditions between particles occur (Hansen et al., 2006). The C-SF was less compacted than the P-SF due to the larger particles present in the co-digested slurry. Thus, the aeration was probably greater, promoting the nitrification process.

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

4. Conclusions

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

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

Acidification of pig and co-digested slurries reduces the loss of TS and VS during storage, compared to non-acidified slurries. This indicates that microbial degradation is decreased by acidification and, thus, more organic matter remains in the slurries at the end of storage. Furthermore, the TAN concentration is significantly reduced in untreated slurries during storage - due to NH_3 volatilization, immobilization, and/or nitrification - but only slightly decreased in acidified slurries and fractions. Therefore, acidified slurries and their fractions have a higher fertilizing value, as less N and organic matter is lost via volatilization and microbial degradation.

Acidification before separation increases the TS and TAN contents in acidified LFs from both types of slurry assayed here, relative to non-acidified LFs, indicating that NH_3 volatilization decreases during separation.

Acidification of pig and co-digested slurries significantly reduces the emissions of NH_3, particularly in the acidified LF, relative to non-acidified fractions.

The highest contribution of the gaseous emissions from the untreated pig and co-digested fractions to the total GHG corresponds to CH_4 from LFs and N_2O from SFs, and these emissions are higher from raw pig slurry than from co-digested fractions. When acidification is applied, emissions of both CH_4 and N_2O are drastically reduced, with co-digested slurry having higher proportional decreases than pig slurry. However, as the total GHG emissions from pig slurry are higher than from co-digested slurry, the reduction in the total gaseous emission is also higher.

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

Acidification applied before separation, as a mitigation practice, can lead to the overall improvement of management practices on farms. It decreases the net total GHG and NH_3 emissions during storage of raw and co-digested pig slurry fractions. More N remains in the slurries, increasing their fertilizer value while reducing environmental pollution and protecting the health of farmers and animals. However, further studies would be required to assess the concentration of alum used in slurries if these are intended to be used as fertilizer.

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

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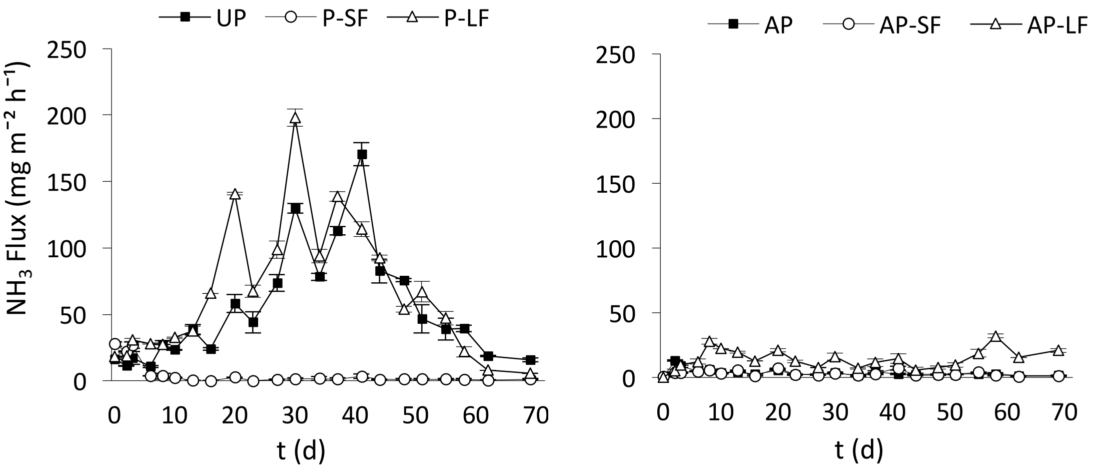
Fig. 1

a) Raw pig slurry



b) Co-digested pig slurry

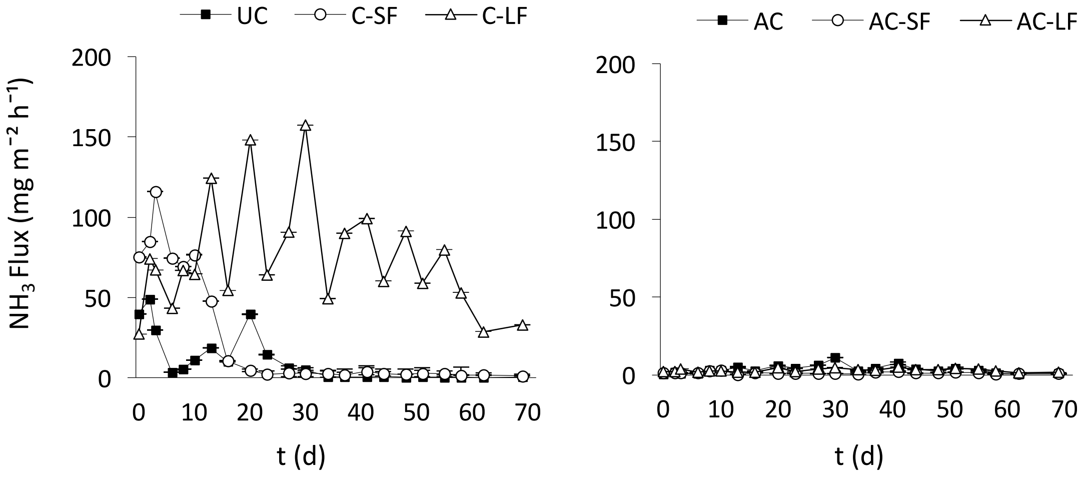
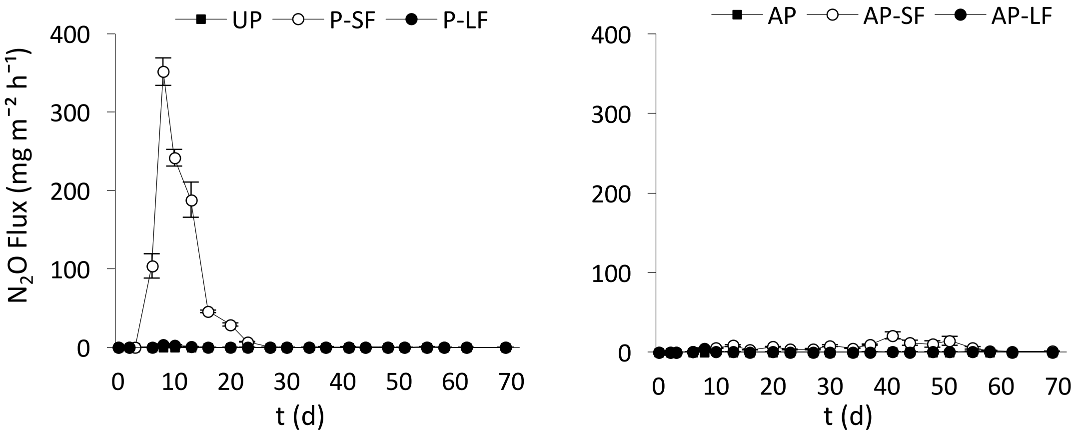


Fig. 2

a) Raw pig slurry



b) Co-digested pig slurry

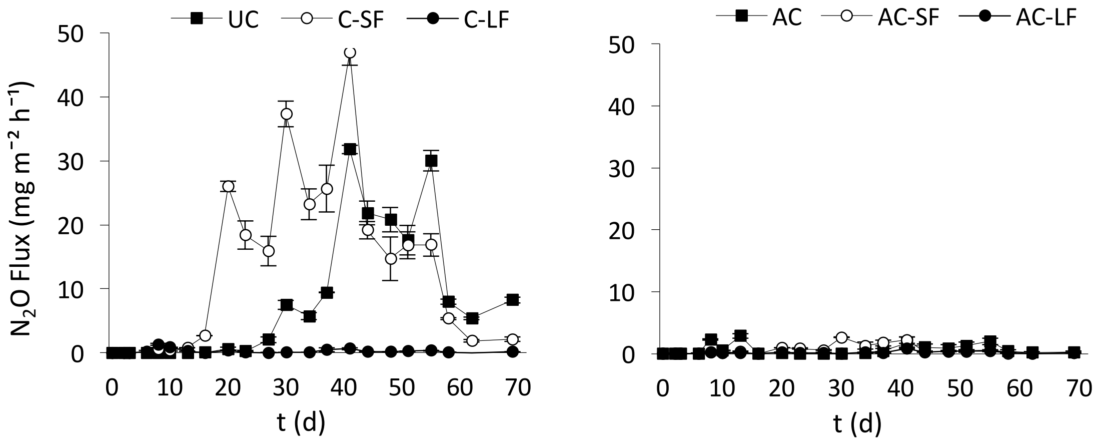
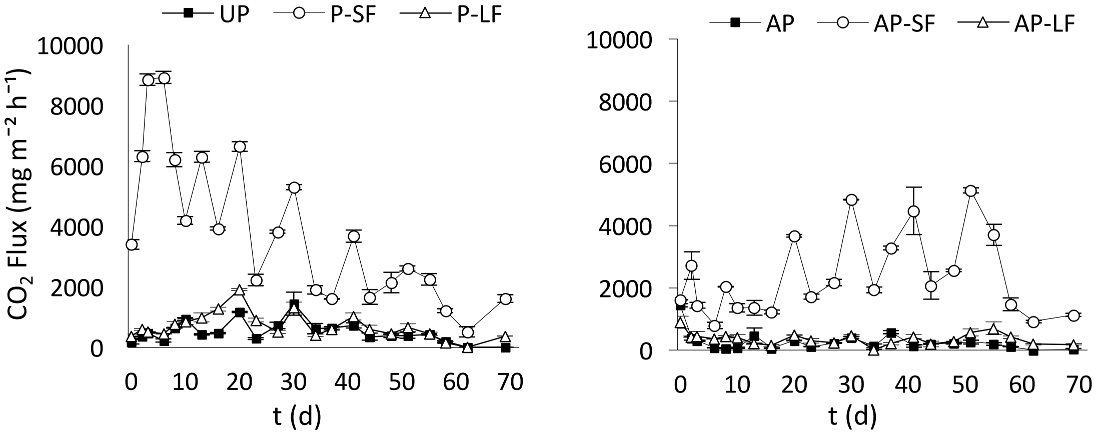


Fig. 3

a) Raw pig slurry



b) Co-digested pig slurry

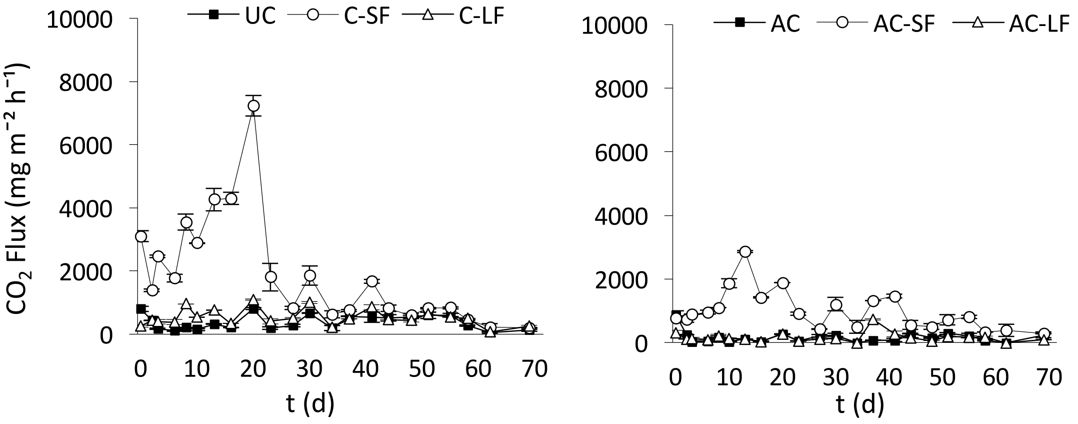
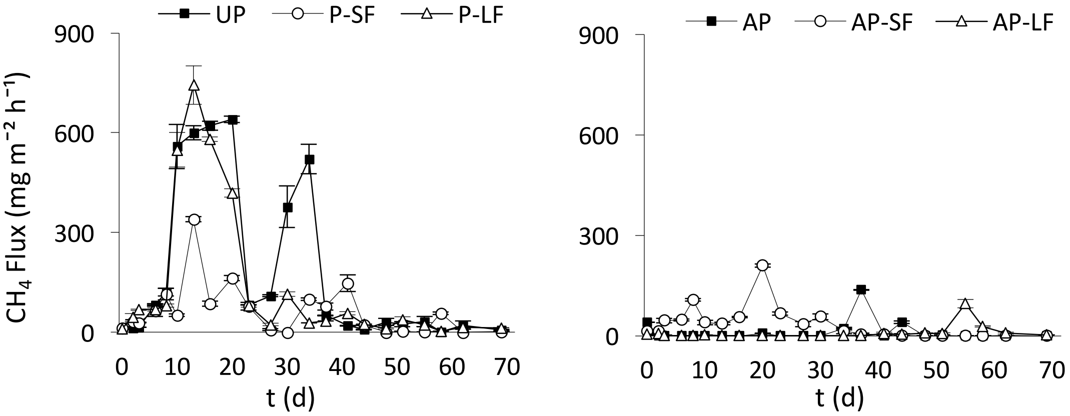


Fig. 4

a) Raw pig slurry



b) Co-digested pig slurry

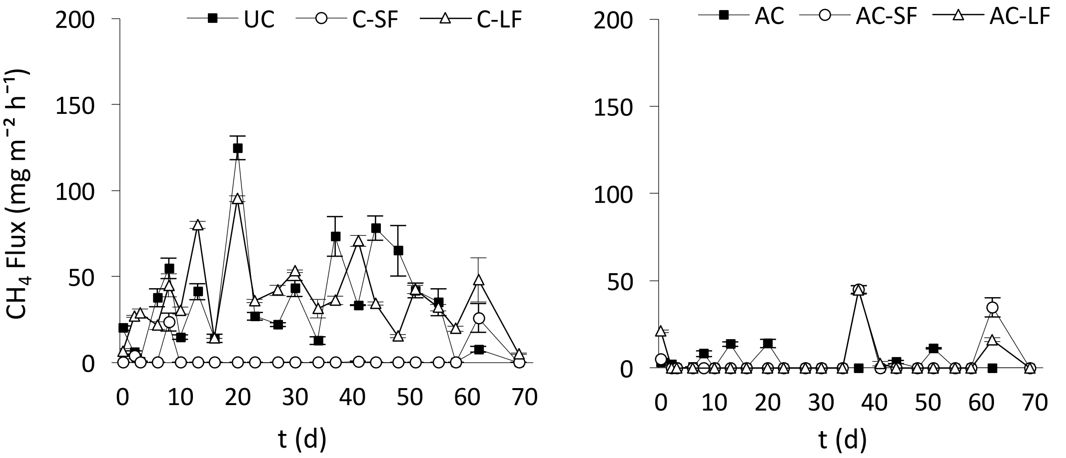
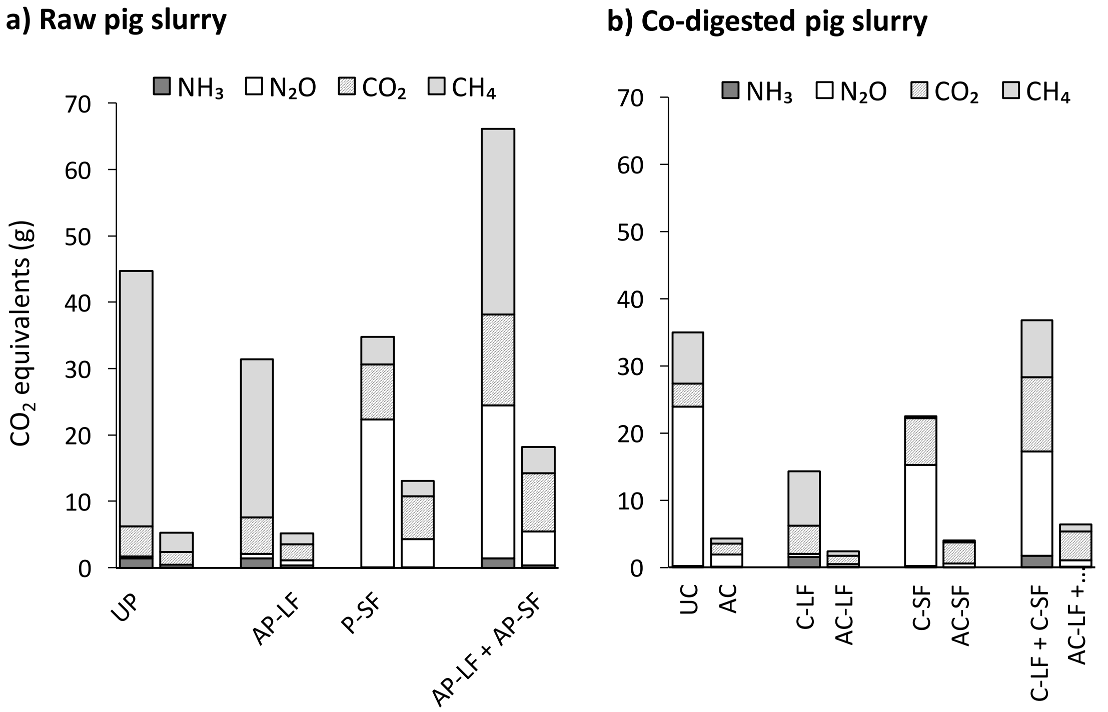


Fig. 5



a) Raw pig slurry

b) Co-digested pig slurry

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

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

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

Table 2. Cumulative emissions of ammonia (NH_3), nitrous oxide (N_2O), carbon dioxide (CO_2), and methane (CH_4) 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_3 are expressed as percentages of initial total nitrogen (TN) and total ammonium nitrogen (TAN) content, emissions of N_2O are expressed as percentages of initial TN and emissions of C (CO_2 and CH_4) 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_3 (% TN)	**U**	18.83^{a} (0.24)	1.04^{c} (0.06)	1.75^{b} (0.08)	1.39^{bc} (0.15)
	LF	25.66^{a} (0.76)	5.07^{c} (0.07)	18.45^{b} (0.16)	0.65^{d} (0.02)
	SF	0.99^{b} (0.06)	1.01^{b} (0.05)	9.80^{a} (0.57)	0.34^{b} (0.01)
N-NH_3 (% TAN)	**U**	31.92^{a} (0.40)	1.75^{c} (0.01)	2.96^{b} (0.08)	1.84^{c} (0.13)
	LF	39.20^{a} (0.20)	7.53^{c} (0.06)	30.77^{b} (0.20)	1.26^{d} (0.08)
	SF	2.00^{b} (0.32)	2.47^{b} (0.02)	26.60^{a} (0.14)	0.84^{c} (0.03)
N-N_2O (% TN)	**U**	0.03^{b} (0.00)	0.04^{b} (0.00)	1.64^{a} (0.07)	0.12^{b} (0.01)
	LF	0.12^{a} (0.01)	0.08^{ab} (0.00)	0.05^{bc} (0.01)	0.04^{c} (0.00)
	SF	9.20^{a} (0.23)	1.89^{c} (0.01)	6.55^{b} (0.22)	0.16^{d} (0.01)
C-CO_2 (% VS)	**U**	7.42^{a} (0.23)	2.07^{c} (0.08)	4.20^{b} (0.31)	1.39^{c} (0.07)
	LF	24.30^{a} (0.08)	6.20^{c} (0.44)	9.69^{b} (0.21)	1.77^{d} (0.03)
	SF	19.28^{a} (0.26)	14.11^{c} (0.07)	17.23^{b} (0.11)	6.18^{d} (0.06)
C-CH_4 (% VS)	**U**	5.83^{a} (0.28)	0.32^{bc} (0.01)	0.87^{b} (0.01)	0.07^{c} (0.01)
	LF	13.24^{a} (0.16)	0.43^{c} (0.03)	1.94^{b} (0.06)	0.10^{c} (0.00)
	SF	0.95^{a} (0.02)	0.49^{b} (0.00)	0.07^{c} (0.00)	0.08^{c} (0.00)

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

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

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

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