



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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ARTICLE INFO

Article history:

Received 14 October 2015

Received in revised form 19 April 2016

Accepted 21 April 2016

Available online 12 May 2016

Keywords:

Acidification

Aluminum sulfate

Pig slurry

Co-digested slurry

Mechanical separation

Gaseous emissions

Storage

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 NH₃, N₂O, CO₂, and CH₄ were followed during 70 days of storage.

Acidification applied before separation significantly reduced the emissions of NH₃ 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, NH₃ and CH₄ emissions were significantly reduced in acidified LFs and N₂O emissions were significantly reduced in acidified SFs. The CO₂ 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.

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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 (NH₃) and greenhouse gases (GHG) such as nitrous oxide (N₂O), methane (CH₄), and carbon dioxide (CO₂), 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 and Blanes-Vidal, 2013). Co-digested slurry contains also large amounts of ammonium (NH₄⁺); thus, NH₃ emissions also occur during storage (Sommer, 1997; Resch et al., 2008).

Acidification of slurries is a treatment known to reduce NH₃ emissions (Stevens et al., 1989; Kai et al., 2008; Fanguero et al., 2015) and recent studies have demonstrated its capacity to reduce CH₄ emissions as well (Petersen et al., 2012; Wang et al., 2014).

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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 (H₂S) emissions (Vandré and Clemens, 1997; Dai and Blanes-Vidal, 2013). Aluminum sulfate (Al₂(SO₄)₃), referred to hereafter as alum, is an acidifying additive which has been used successfully to reduce NH₃ 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; Regueiro et al., 2016). 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 NH₃, CO₂, CH₄, and N₂O 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 °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 (NH₄⁺) content. The TN content was analyzed by the Kjeldahl method (Horneck and Miller, 1998). The TS content was determined after drying 10 g of fresh material at 105 °C to constant weight for 24 h and the VS content by loss on ignition after calcination at 550 °C for 3 h (APHA, AWWA, and WEF, 2005). The total NH₄⁺ content was analyzed after extraction with 30 mL of 0.05 M CaCl₂ (Van Raij, 1998; Houbba 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 NH₃, CO₂, CH₄, and N₂O were measured by the dynamic chamber method described in Berg et al. (2006).

The vessels were closed 30 min 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, CO₂, and N₂O and cross compensation (Dinuccio et al., 2008). The gas concentrations at the outlet were recorded for 16 min, 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 8–30, and every two days during the remaining period. Gas fluxes were calculated according to Eq. (1) as follows:

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

where F (mg m⁻² h⁻¹) is the gas flux, Q is the airflow rate (m³ h⁻¹) dosed to the vessels, C_{in} (mg m⁻² h⁻¹) is the gas concentration in the

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