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Acidification with sulfur of the separated solid fraction of raw and co-digested pig slurry: effect on GHG and ammonia emissions during storage

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Abstract

A study was performed to assess: i) the feasibility to acidify the separated solid fraction of raw and co-digested pig slurry by using a powdery sulfur-based product and ii) the effect of this acidification method on greenhouse gases and ammonia emissions during manure storage. Samples of raw and co-digested pig slurry were collected at two commercial farms and mechanically separated by a lab-scale screw press device. The sulfur powder (80% concentration) was added to the obtained separated solid fractions at three application rates: 0.5%, 1 % and 2% (w/w). Carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and NH_3 emissions were afterwards measured during storage of the acidified samples and compared to those measured from untreated samples (control). Gaseous emissions were determined with dynamic chamber method by Infrared Photoacoustic Detection. Gaseous losses were monitored along 30 and 60 days of storage time for raw solid fraction and digested solid fraction respectively. The addition of the tested sulfur powder to solid fractions showed to be a reliable and effective method to acidify raw and co-digested solid fractions. Results showed a significant reduction of both greenhouse gases and ammonia emission regardless of the separated solid fraction type. The highest sulfur application rate (2% w/w) led to a reduction of up to 78% of GHG emission and 65% of NH_3 losses from raw separated solid fraction when compared to control. Similar results were achieved from the co-digested solid fraction, with emission reduction of up to 67% for NH_3 and 61% for GHG.

Introduction

Gaseous losses of pollutants to the atmosphere are a major problem associated with animal manure management. In 2011 the agricultural sector contributed 94% to total ammonia (NH_3) emission in Europe (European Environment Agency, 2014). According to Oenema (2007), 52% of excreted N is available as crops nutrient, meaning nearly half excreted N is lost along the manure management chain. Barns and slurry stores represent up to 80% of the total NH_3 losses from agricultural activities (Anderson *et al.* 2003).

Greenhouse gas (GHG) losses from manure management, i.e. methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O), account for 15% of total agricultural emissions in Europe (10% of total anthropogenic GHG emissions) (European Environment Agency, 2013). In recent years many studies validated methods for the reduction of GHG emission from manure storage such as floating covers (Balsari *et al.* 2013; Dinuccio *et al.* 2012; Balsari *et al.* 2006), natural crust (Sommer *et al.*

2000), perlite and lightweight expanded clay aggregate (Leca®) (Berg *et al.* 2006), wooden lids and chopped straw placed on the slurry surface (Amon, 2006).

A strategy widely used in Denmark to reduce NH_3 volatilization consists in slurry acidification (Eriksen *et al.* 2008). Ammonia volatilization can indeed be reduced by lowering slurry pH, whereby the NH_3/NH_4^+ equilibrium shifts towards NH_4^+ concentration. Acidification is also known to positively affect GHG emission (Fangueiro *et al.* 2014; Dai & Blanes-Vidal, 2013; Kai *et al.* 2008; Jensen, 2002; Frost *et al.* 1990; Stevens *et al.* 1989).

Nevertheless, acidification is commonly performed by using strong acids, mainly concentrated sulfuric acid. Some limitations to their use, such as their hazards to human health, are important issues that need to be overcome. Furthermore, at present, solutions to acidify solid manures (e.g. farmyard manure and slurry separated solid fraction) are lacking.

The paper presents the results of a laboratory study performed to assess: i) the feasibility to acidify the separated solid fraction of raw and co-digested pig slurry by using a powdery sulfur-based product and ii) the effect of this acidification method on greenhouse gases (CO_2, CH_4, N_2O) and NH_3 emissions during manure storage.

Materials and methods

Manure sampling

Samples of raw (RS) and co-digested slurry (DS) were sampled at two farms located in Piedmont (northwest Italy).

Raw slurry was collected from a pig-breeding farm, where 2500 sows and 2300 fattening pigs were bred on slatted floors. The pigs' diet was mainly represented by corn mash, and to lesser degrees, of barley, soybean, wheat, and bran.

Co-digested slurry was collected in the same period from a CSTR (Continuous Stirred Tank Reactor) biogas plant with an installed electric power of 500 kW. The mesophilic plant (40° C) has a hydraulic retention time (HRT) of 40 days and is fed with (w/w) 70% pig slurry, 12% maize silage, 7% sorghum silage and 4% cattle manure.

Raw slurry and co-digestate were transported in 30 litres barrels to the laboratory and placed in a refrigerated room at +4° C until separation tests.

Mechanical separation

Separation tests were performed at the Waste Management Group laboratory of the Department of Agriculture, Forest and Food Sciences (DISAFA) - University of Turin, Italy. Raw slurry and co-digested slurry were mechanically separated by a lab-scale screw press device normally used to produce tomato sauce (Popovic *et al.* 2014). The machinery has a maximum working rate of 200 kg h^{-1} of tomato, an auger rotation of 180 rpm and a 1 mm diameter mesh size. Screen openings of commercial mechanical separators vary, ranging from 0.1 to 3.0 mm, according to separator type and particularly to the total solids content of the input manure (Hjorth *et al.* 2010). For screw press, studies conducted in Italy by Balsari *et al.* (2006) and Dinuccio *et al.* (2014) reported screen openings ranging from 0.75 to 1.5 mm, with smaller openings typically used for pig slurry and larger for dairy cattle.

Solid fraction acidification and chemical analysis

The efficiency of acidification on emission abatement depends on the additive, manure type, step in the slurry management chain, and contact between additive and manure (Ndegwa *et al.* 2008). Several studies have confirmed that NH_3 emissions are directly related to the final pH of the slurry reached after the addition of the amendment (Fangueiro *et al.* 2014): by achieving pH values of 5.5 – 6 the NH_3 (Kai *et al.* 2008; Jensen, 2002; Frost *et al.* 1990; Stevens *et al.* 1989) and CH_4 (Ottosen *et al.* 2009) emissions can be reduced by 70 - 90%. Thus, we fixed the value 5.5 as pH target below which emission were expected to be decreased.

The obtained undigested (raw) and co-digested solid fractions were acidified by the addition of a powdery sulfur-based product (Microthiol® Disperss®, 80% micronized wettable elemental sulfur) widely used in crop protection as a fungicide.

The rationale behind acidification with elemental sulfur relies on the chemical reaction described in equation (1):

$$S^0 + ½\, O_2 + 2H_2O \Leftrightarrow CH_2O + 2H^+\, SO_4^{2-} \qquad (1)$$

It has been well documented (e-g., Fukumoto *et al.* 2003) that manure that is stored solid allows oxygen diffusion into the manure pile, and therefore, there will likely be the opportunity reaction of equation 1 to occur.

Sulfur was added to both co-digested and raw separated solid fractions at three rates: 0.5%, 1 % and 2% (w/w) calculated on wet basis (WB). Solid fraction after sulfur addition was thoroughly mixed manually to evenly distribute the powdery product. Unacidified raw and co-digested solid fractions were used as control. Prior to and after acidification, samples of all treatments were collected, and stored at 4°C prior to chemical characterization. Dry matter (DM) content was measured after drying (24h at 105 °C) the fresh samples to constant weight. The volatile solids content (VS) was calculated as weight loss upon ignition at 550 °C for 5h (VDI 4630, 2006). Samples were weighted using a four digits trusted balance (Kern®, mod. ABS 220-4). pH of the solid fractions prior and during the experiment were measured by a glass electrode for semi solid-biomasses (Hanna instruments® electrode HI 1053B). At the end of the trials pH was measured after solid fraction dilution in deionized water, followed by 45 min of shaking, and then 15 min of settling (Jorgensen & Jensen, 2009). Total N (N_{tot}) and total ammonia nitrogen (N-NH_3) were measured according to the Kjeldahl standard method (AOAC, 1990).

Measurement of gaseous emission

Emission tests were performed by filling 2000cm^3 jars with 1000cm^3 of unacidified and acidified solid fractions with three replicates per treatment. The bulk density of the tested raw and co-digested solid fraction samples was estimated to be 500g/1000cm^3. Gaseous (CO_2, CH_4, N_2O and NH_3) emissions were measured by a ventilated chamber system and using an infrared photo acoustic detector (IPD) (1412 Multi-gas Monitor, Innova® Air Tech Instruments, Ballerup, Denmark) as described by Dinuccio *et al.* (2008). The IPD was calibrated before the beginning of the experiment by the manufacturer and was run with corrections from cross interferences between CO_2-water vapor and measured target gases, and cross compensation (Huszár *et al.* 2008; Tirol-Padre *et al.* 2014). Before emission measurements, each jar was closed with an airtight lid provided with two ports for air inlet and outlet. The air inlet port was connected in an airtight way with a flow meter and a pump. The headspace between the solid-fraction surface and the lid was then ventilated to guarantee a complete air change per minute. Gaseous emission were monitored every 24h for the first 2 weeks of trial and three times per week thereafter. The operative steps followed for emission measurement was carried out according to Dinuccio *et al.* (2008). Specifically, an air flow of 1000 cm^3/min across the headspace was established for at least 20 min before gas sampling to reach a steady state and then emissions were measured over a period of 16 min. Trials were stopped when all (GHG and NH_3) gaseous emission dropped to zero for three consecutive days. Specifically, the tests lasted 30 and 60 days for raw and co-digested solid fraction respectively. The cumulative net gaseous emissions were determined according to Dinuccio *et al.* (2008). Data were tested by one-way ANOVA and the Tukey tests (α = 0.05). Measured gaseous losses were converted into CO_2eq by using the IPPC (2013) Global Warming Potential (GWP) values. Along the experiment, the environmental temperature at the laboratory was recorded by means of two Onset® Hobo U12 data loggers.

Results and discussion

Raw and co-digested solid fractions chemical characteristics

Chemical characteristics of raw and co-digested solid fraction samples measured at the beginning of the experiments are shown in Table 1. Despite a similar DM content, VS concentration in the co-digested solid fraction was significantly ($p<0.05$) lower than that in raw solid fraction, as a consequence of organic matter degradation during the anaerobic digestion process. The initial pH were 8.00 and 8.51 for the raw and co-digested solid fraction respectively. Also total nitrogen concentration was similar for the two biomasses, whereas a higher ammonia nitrogen content was found for the co-digested solid fraction, due to N mineralization occurring during anaerobic digestion.

At the end of the experiment, the DM content of both raw and co-digested solid fraction were found to be higher compared to the initial values (Table 2) as a consequence of water evaporation during the experiments (Table 3). The evolution of solid fractions pHs along the experiments are shown in Fig. 1. With respect to unacidified solid fraction from mechanical separation of raw slurry, pH remained above 6.5 for the whole experimental period. Acidified fractions showed decreasing pH values already after 24hrs from sulfur addition, as a result of H^+ formation and S oxidation (Roig *et al.* 2004). Sample RS 2 reached the pH target (5.5) at day 7, RS 1 at day 9 and RS 0.5 after 14 days from S addition. The minimum pH values (2.47) was reached by RS2 at day 23. With co-digested solid fractions, sulfur addition took longer to affect solid fraction pHs. The latter started indeed to drop after three days from acidification. This might be due to the higher buffer capacity of the material when compared to non-digested solid fraction. DS 1 and DS 2 needed about a week to reach the pH target, whereas pH of DS 0.5 treatment dropped below 5.5 after approximately 30 days. The minimum pH value (2.87) was reached by DS2 treatment at day 56.

Environmental temperature is well known to strongly affect NH_3 and CH_4 emissions (Dinuccio *et al.* 2008, Wang *et al.* 2014). Furthermore, Jaggi *et al.* (1999) found a strong influence of temperature on the rate of S oxidations. Recorded temperatures were similar along the two experiments. Average, minimum and maximum values are reported in Table 3.

NH_3 emissions

NH_3 emissions from raw-slurry separated solid fraction started to drop already at day 3 when pH approached 5.5 (Fig. 2a). All treatments were effective, regardless of S application rate. Fig. 3 shows the total NH_3 emission quantified along the trial. The control (RS) lost as ammonia approximately 6% of its initial total nitrogen content (Table 4). This value is consistent with that (5.6%) measured by Dinuccio *et al.* (2008). Acidified samples lost 1.93% to 3.20% of their initial total nitrogen (Table 4). Depending on the amount of added S, NH_3 emissions from RS 0.5, RS 1 and RS 2 acidified fractions were respectively 49%, 65% and 70% lower than those of the control treatment. Specifically, the higher the S application rate, the higher the abatement efficacy. These findings are consistent with measurement performed on raw slurry by Pain *et al.* (1990), Kai *et al.* (2008) and Dai & Blanes-Vidal (2013) by using sulfuric acid as acidifying agent. The NH_3 emissions from co-digested solid fraction were twofold higher when compared to those of raw separated solid fraction. This was probably due the higher initial N-NH_3 concentration (Table 1) (Chadwick *et al.* 2011). All acidification treatments significantly reduced ammonia emissions by approximately 65% with respect to untreated solid fraction. NH_3 emissions from acidified fractions started to drop at day 7 (Fig. 2b), when pH approached 5.5 (Fig. 1b). The control (DS) lost on average 19% of total initial nitrogen as ammonia, whereas from acidified solid fractions 6-7% of the initial nitrogen was lost as ammonia (Table 4).

GHG emissions

The effect of S addition on GHG emissions from the storage of raw slurry and co-digested solid fractions is displayed in Fig. 4. Although the two tests had different duration (30 and 60 days for RSs and DSs respectively) total GHG emission from control samples (RS, DS) were in the range of 6 kg CO_2eq m^{-2}. N_2O was the most relevant GHG in both experiments. Acidification showed to be more effective when applied on raw (non-digested) solid fractions. The highest emission reduction (%) was obtained with 2% S addition, but this value was found to be not significantly ($p > 0.05$) different from that (%) recorded for RS 1. A 0.5% S application rate was able to reduce by 44% GHG emission when compared to control. The same S application rate (treatment DS 0.5) increased CO_2eq. emission by 44% when applied to co-digested solid fraction, due to high (+55%) N_2O emissions. Nevertheless, DS 0.5 reached the target pH very late (after 30 days from S addition), thus suggesting this rate to be too low for this kind of animal waste, being characterized by a high initial pH and buffer capacity. N_2O emissions increasing were probably due to an enhanced microbial activity with S as a growing factor (Sierra-Alvarez *et al.* 2007). Biogas obtained by digesting pig slurry generally contains approximately 3000-8000 ppm hydrogen sulfide (H_2S) (Wei-Chin Lin *et al.* 2012). Hydrogen sulfide have damaging effects on the engine components and equipment and it is therefore removed before combustion in combined heat and power units. The most common method for H_2S removal from biogas is based on the addition of a small amount of oxygen or air (3-5% v/v) directly into the digester (Ramos & Fdz-Polanco, 2014). In this way it takes place the biological aerobic oxidation of H_2S to elemental sulfur and sulphates by a consortium of sulphur-oxidising microorganisms (e.g., Thiobacillus bacteria). This process can results in the accumulation of elemental sulfur and sulphates in the digester. It is assumed that in the co-digested slurry are present nitrifying prokaryotes that could have an affinity with sulfur. Therefore a higher sulfur dose might be necessary to inhibit the nitrification/denitrification biological activity of these bacteria that could be otherwise promoted by a lower S application rate.

Higher S application rates (DS 1 and DS 2) significantly reduced CO_2eq. losses (by 39% and 55% respectively). With special regards to methane, by applying 2% sulfur a 54% losses reduction was observed.

Conclusions

The addition of elemental S to solid fractions showed to be a reliable and effective method to acidify raw and digested solid fractions. Thus, it can be considered as an alternative method to the common sulfuric acid utilization. Sulfur addition led to significant reduction of gaseous losses (NH_3 and GHG) during the solid fractions storage. The most evident outcome is represented by the significant reduction of NH_3 emissions rate for both the tested biomasses with abatement of up to 70% in raw slurry solid fraction and 65% for the digested one.
GHG emissions were respectively reduced from 44% to 78% according to the amount of S added to non-digested solid fraction. The lower S rate significantly increased GHG emission from the digested solid fraction only with special regards to increased N_2O losses.
The experimental results allow a first positive evaluation on the possibility to decrease the pH and gaseous emissions by adding sulfur to solid manures, thus enabling an effective pollution reduction without using strong acids. The latter aspect is indeed one of the main concerns and a major limit to the diffusion of manure acidification at a European level.
According to our preliminary results 1% S might be considered as the best application rate, allowing an emission reduction in line with the present acidification technology performances (Fangueiro *et al.* 2014). However, according to the current market price of powdery sulfur for crop protection purpose (1€/kg) the former application rate would cost around 5€ per ton of treated solid fraction. This cost is five times higher than that of slurry acidification by H_2SO_4. Nevertheless, it must be considered that besides the commercial powdery sulfur (normally used for crop protection), sulfur is a byproduct of the oil refining process. The latter is considered as a waste and thus its reuse in the animal waste management sector might considerably reduce the cost of slurry acidification. Appropriate procedures for safely using a powdery acidifying product are already under study by our research group. Moreover, the DISAFA-Waste Management Group is currently investigating the feasibility to lower solid fraction pH by S addition to slurry prior to mechanical separation, with the aim to i) reduce the S application rates and, ii) acidify both solid and liquid fractions with a single treatment.

References

Amon B, Kryvoruchko V, Amon T (2006) Influence of different methods of covering slurry stores on greenhouse gas and ammonia emissions. In: *International Congress Series: Greenhouse Gases and Animal Agriculture: An Update* **1293,** 315–318.

Anderson N, Strader R, Davidson C (2003) Airborne reduced nitrogen: ammonia emissions from agriculture and other sources. *Environment International* **29,** 277-286.

Balsari P, Dinuccio E, Gioelli F (2013) A floating coverage system for digestate liquid fraction storage. *Bioresource Technology* **134,** 285–289.

Balsari P, Dinuccio E, Gioelli F (2006a) A low cost solution for ammonia emission abatement from slurry storage. In: *International Congress Series: Greenhouse Gases and Animal Agriculture: An Update* **1293,** 323–326.

Balsari P, Gioelli F, Dinuccio E, Santoro E (2006b) Monitoraggio degli impianti di separazione solido liquido dei liquami di suini e di bovini (Monitoring and assessment of different devices for mechanical separation of pig and cattle slurries). *Department of Agriculture, Forestry and Food Sciences (DISAFA), Internal report***,** 166 p.

Berg W, Brunsch R, Pazsiczki I (2006) Greenhouse gas emissions from covered slurry compared with uncovered during storage. *Agriculture, Ecosystem and Environment* **112**, 129–134.

Chadwick D, Sommer S, Thorman R, Fangueiro D, Cardenas L, Amon B, Misselbrook T (2011) Manure management: Implications for greenhouse gas emissions. *Animal Feed Science and Technology* **166–167,** 514–531.

Dai XR, Blanes-Vidal V (2013) Emissions of ammonia, carbon dioxide, and hydrogen sulfide from swine wastewater during and after acidification treatment: Effect of pH, mixing and aeration. *Journal of Environmental Management* **115,** 147–154.

Dinuccio E, Gioelli F, Balsari P (2014) Prove di separazione meccanica del liquame suino tal quale e co-digerito (Mechanical separation of raw and co-digested pig slurries). In ´Sostenibilità ambientale ed economica: la gestione degli effluenti negli allevamenti di suini´. (Eds P Bonfanti, G Provolo) pp. 29-37. (Forum Editrice Universitaria Udinese S.r.l.).

Dinuccio E, Gioelli F, Balsari P, Dorno N (2012) Ammonia losses from the storage and application of raw and chemo-mechanically separated slurry. *Agriculture, Ecosystems and Environment* **153**, 16–23.

Dinuccio E, Berg W, Balsari P (2008) Gaseous emissions from the storage of untreated slurries and the fractions obtained after mechanical separation. *Atmospheric Environment* **42**, 2448–2459.EEA (2014) Ammonia (NH_3) emissions (APE 003). Copenhagen, Denmark. http://www.eea.europa.eu/data-and-maps/indicators/eea-32-ammonia-nh3-emissions-1/assessment-4 (accessed: 01.14.).

EEA (2013) Annual European Union greenhouse gas inventory 1990–2011 and inventory report 2013; submission to the UNFCCC secretariat. Copenhagen, Denmark. http://www.eea.europa.eu//publications/european-union-greenhouse-gas-inventory-2013 (accessed: 01.14.).

Eriksen J, Sorensen P, Elsgaard L (2008) The fate of sulfate in acidified pig slurry during storage and following application to cropped soil. *Journal of Environmental Quality* **37,** 280–286.

Fangueiro D, Hjorth M, Gioelli F (2015) Acidification of animal slurry - a review. *Journal of Environmental Management* **149**, 46-56.

Frost JP, Stevens RJ, Laughlin RJ (1990) Effect of separation and acidification on ammonia volatilization and on the efficiency of slurry nitrogen for herbage production. *Journal of Agricultural Science* **115**, 49–56.

Fukumoto Y, Rom HB, Dahl P (2003) Relationship between gas depth profiles in compost heap and gas emission. *Agricultural Engineering International* **5** (EE 03 004), 1–13.

Hjorth M, Christensen KV, Christensen ML, Sommer SG (2010) Solid–liquid separation of animal slurry in theory and practice. A review. *Agronomy for Sustainable Development* **30**, 153–180.

Huszár H, Pogány A, Bozóki Z, Mohácsi Á, Horváth L, Szabó G (2008) Ammonia monitoring at ppb level using photoacoustic spectroscopy for environmental application. *Sensors and Actuators B* **134**, 1027-1033.

IPCC (2013) Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker TF, Qin D, Plattner GK, Tignor M, Allen SK, Boschung J, Nauels A, Xia Y, Bex V, Midgley PM (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp.

Jaggi RC, Aulakh MS, Sharma R (1999) Temperature effect on soil organic sulphur mineralization and elemental sulphur oxidation in subtropical soils of varying pH. *Nutrient Cycling in Agroecosystems* **54,** 175-182.

Jensen AO (2002) Changing the environment in swine buildings using sulfuric acid. *Transactions of the ASAE* **45,** 223–227.

Jorgensen K, & Jensen LS (2009) Chemical and biochemical variation in animal manure solids separated using different commercial separation technologies. *Bioresource Technology* **100,** 3088-3096.

Kai P, Pedersen P, Jensen JE, Hansen MN, Sommer SG (2008) A whole-farm assessment of the efficacy of slurry acidification in reducing ammonia emissions. *European Journal of Agronomy* **28,** 148–154.

Ndegwa PM, Hristov AN, Arogo J, Sheffield RE (2008) A review of ammonia emission mitigation techniques for concentrated animal feeding operations. *Biosystems Engineering* **100,** 453-469.

Oenema O, Oudendag D, Velthof L (2007) Nutrient losses from manure management in the European Union. *Livestock Science* **112,** 261-272.

Ottosen LDM, Poulsen HV, Nielsen DA, Finster K, Nielsen LP, Revsbech NP (2009) Observations on microbial activity in acidified pig slurry. *Biosystems Engineering* **102,** 291–297.

Pain BF, Thompson RB, Rees YJ, Skinner JH (1990) Reducing gaseous losses of nitrogen from cattle slurry applied to grassland by the use of additives. *Journal of the Science of Food and Agriculture* **50,** 141–153.

Popovic O, Gioelli F, Dinuccio E, Balsari P (2014) Improved pig slurry mechanical separation using chitosan and biochar. *Biosystems engineering* **127,** 115-124.

Ramos I, Fdz-Polanco M (2014) Microaerobic control of biogas sulphide content during sewage sludge digestion by using biogas production and hydrogen sulphide concentration. *Chemical Engineering Journal* **250,** 303–311.

Roig A, Cayuela ML, Sanchez MA (2004) The use of elemental sulphur as organic alternative to control pH during composting of olive mill wastes. *Chemosphere* **57,** 1099-1105.

Sierra-Alvarez R., Beristan-Cardoso R., Salazar M., Gomez J., Razo-Florez E., Field JA (2007) Chemolithotrophic denitrification with elemental sulfur for groundwater treatment. *Water Research* **41**, 1253 – 1262.

Sommer SG,. Petersen SO, Sogaard HT (2000) Greenhouse gas emission from stored livestock slurry. Journal of Environmental Quality **29,** 744–751.

Stevens RJ, Laughlin RJ, Frost JP (1989) Effect of acidification with sulphuric acid on the volatilization of ammonia from cow and pig slurries. *Cambridge Journal of Agricultural Science* **113,** 389–395.

Tirol-Padre A, Rai M, Gathala M, Sharma S, Kumar V, Sharma PC, Sharma DK, Wassmann R, Ladha J (2014) Assessing the performance of the photo-acoustic infrared gas monitor for measuring CO_2, N_2O, and CH_4 fluxes in two major cereal rotations. *Global Change Biology* **20**, 287–299.

Wang K, Huang D, Ying H, Luo H (2014) Effects of acidification during storage on emissions of methane, ammonia, and hydrogen sulfide from digested pig slurry. *Biosystems Engineering* **122,** 23–30.

Wei-Chih Lin, Yu-Pei Chen, Ching-Ping Tseng (2012) Pilot-scale chemical–biological system for efficient H_2S removal from biogas. *Bioresource Technology* **1355,** 283-291.

Table captions

Table 1. Average chemical characteristics of raw and co-digested solid fractions at the beginning of the experiments (n=3). Values of Standard deviation in brackets.

Table 2. Average chemical characteristics of the solid fraction at the end of the test (n=3). Values of Standard deviation in brackets.

Table 3. Average, maximum and minimum temperatures measured during the tests.

Table 4. Percentage of ammonia nitrogen emitted from raw slurry SF and digested solid fractions, values with same letters are not significantly different, (n=3). Values of Standard deviation in brackets.

Table 1.

Biomass	**DM (%)**	**VS (% DM)**	**pH**	**N_{tot} (%w/w)**	**N-NH_3 (%Ntot)**
Pig slurry	15.4 (0.16)	88.0 (0.14)	8.00 (0.01)	0.32 (0.09)	27.0 (0.07)
Co-digested	14.2 (0.32)	83. 7 (0.33)	8.51 (0.02)	0.30 (0.10)	36.0 (0.11)

DM: dry matter, VS: volatile solids, N_{tot}: total nitrogen, N-NH_3: ammonia nitrogen

Table 2.

Sample	**DM (%)**	**VS (% DM)**	**pH**	**N_{tot} (%w/w)**	**N-NH_3 (%Ntot)**
RS	23.4 (1.20)	85.2 (0.42)	7.14 (0.02)	0.54 (0.12)	1.00 (0.05)
RS 0.5	27.5 (2.70)	84.9 (0.11)	6.18 (0.10)	0.77 (0.06)	45.0 (0.12)
RS 1	28.5 (2.15)	80.6 (0.84)	4.65 (0.35)	0.88 (0.11)	53.0 (0.08)
RS 2	29.7 (2.51)	88.9 (0.51)	3.55 (0.28)	1.32 (0.08)	57.0 (0.12)
DS	26.5 (1.76)	80.0 (0.44)	7.77 (0.11)	0.54 (0.05)	2.00 (0.00)
DS 0.5	30.1 (3.65)	80.1 (0.66)	5.88 (0.18)	0.68 (0.10)	30.0 (0.06)
DS 1	33.8 (3.64)	80.7 (0.49)	4.63 (0.36)	0.85 (0.14)	51.0 (0.03)
DS 2	36.1 (2.19)	81.1 (0.44)	3.51 (0.23)	0.92 (0.10)	55.0 (0.13)

Table 3.

Origin of solid fraction	**Average (°C)**	**Max (°C)**	**Min (°C)**
Pig slurry	20.5	24.1	15.5
Co-digested slurry	21.3	26.5	15.5

Table 4.

Trial	N_NH3 emitted (%Ntot)
RS	6.34 (0.94) b
RS 0.5	3.20 (0.29) a
RS 1	2.24 (0.05) a
RS 2	1.93 (0.40) a
DS	19.2 (1.08) b
DS 0.5	7.27 (0.84) a
DS 1	6.09 (0.55) a
DS 2	6.30 (0.78) a

Figures captions

Fig. 1. Average pH values pattern of (a) raw slurry solid fraction and (b) co-digested solid fraction samples along the experiment

Fig. 2. Emission fluxes of ammonia (NH_3) during storage of (a) raw slurry solid fraction and (b) co-digested solid fraction. Error bars indicate standard deviation (number of observations=3)

Fig. 3. Total net ammonia emission from (a) raw slurry solid fraction and (b) digested solid fraction (values with same letters are not significantly different)

Fig. 4. Total GHG emissions during a) raw pig slurry solid fractions and b) co-digested solid fractions storage (values with the same letters are not significantly different, n=3)

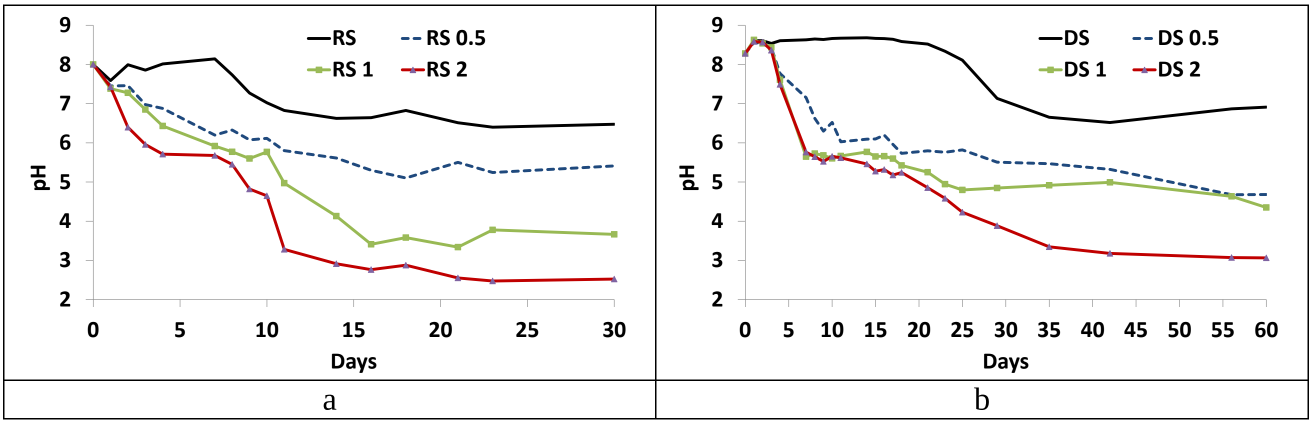

Fig. 1.

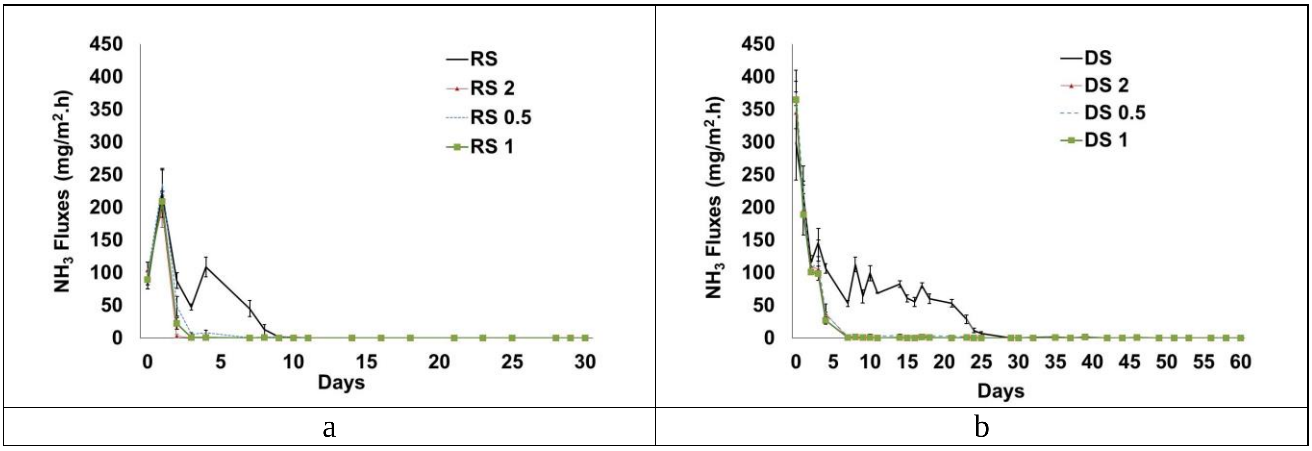

Fig. 2.

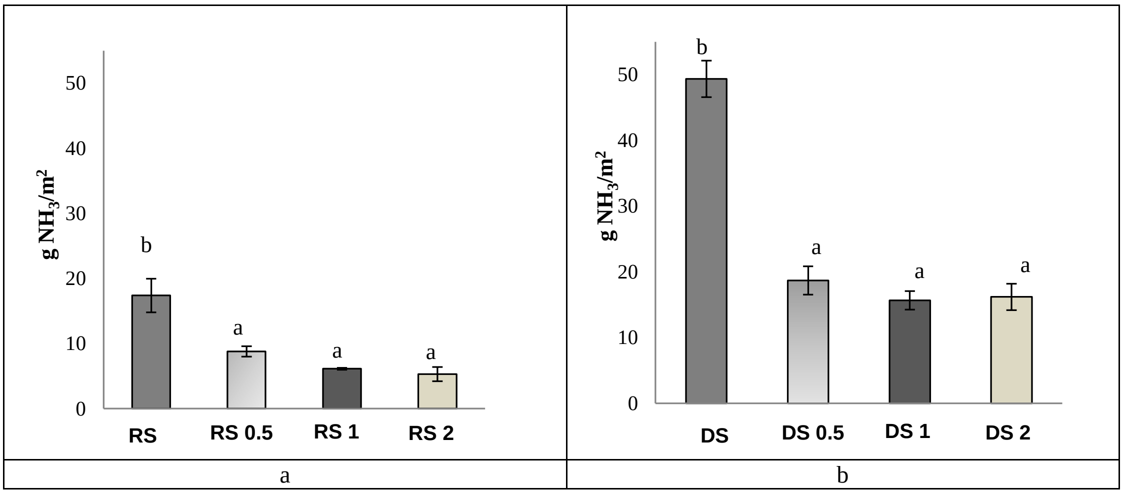

Figure 3.

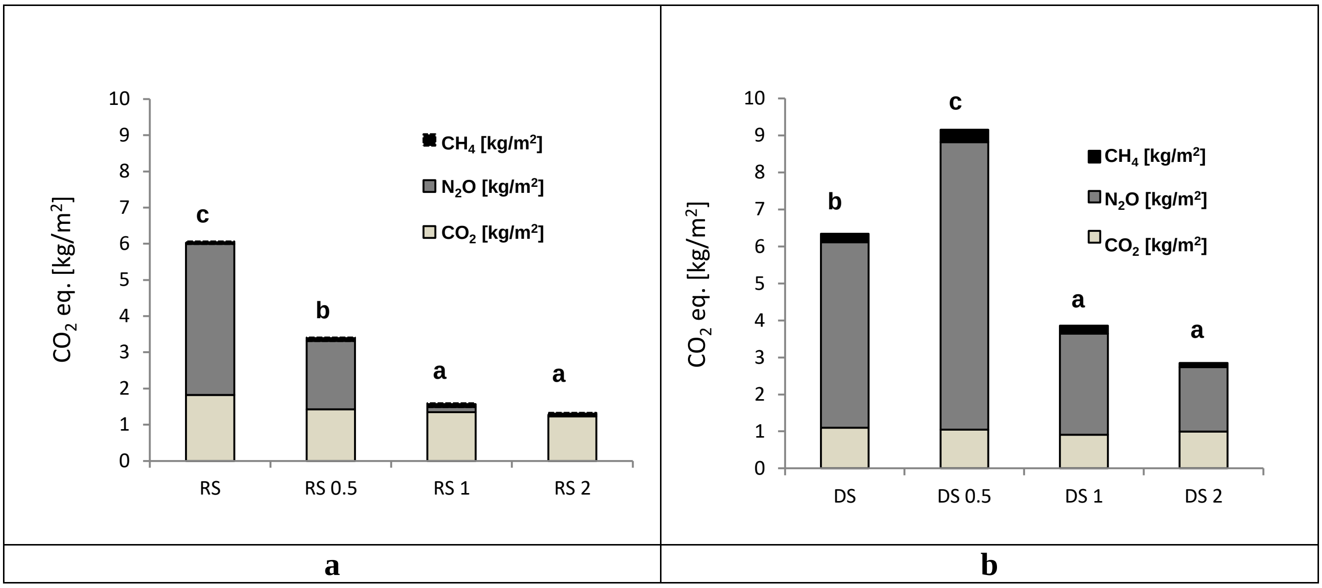

Fig. 4.