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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 (CO₂), methane (CH₄), nitrous oxide (N₂O) and NH₃ 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 NH₃ 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 NH₃ 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 (NH₃) 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 NH₃ losses from agricultural activities (Anderson *et al.* 2003).

Greenhouse gas (GHG) losses from manure management, i.e. methane (CH₄), carbon dioxide (CO₂) and nitrous oxide (N₂O), 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 NH₃ volatilization consists in slurry acidification (Eriksen *et al.* 2008). Ammonia volatilization can indeed be reduced by lowering slurry pH, whereby the NH₃/NH₄⁺ equilibrium shifts towards NH₄⁺ 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 (CO₂, CH₄, N₂O) and NH₃ 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

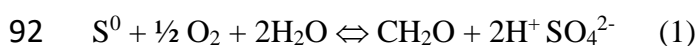
77 openings ranging from 0.75 to 1.5 mm, with smaller openings typically used for pig slurry and
78 larger for dairy cattle.

79 *Solid fraction acidification and chemical analysis*

80 The efficiency of acidification on emission abatement depends on the additive, manure type, step in
81 the slurry management chain, and contact between additive and manure (Ndegwa *et al.* 2008).
82 Several studies have confirmed that NH₃ emissions are directly related to the final pH of the slurry
83 reached after the addition of the amendment (Fangueiro *et al.* 2014): by achieving pH values of 5.5
84 – 6 the NH₃ (Kai *et al.* 2008; Jensen, 2002; Frost *et al.* 1990; Stevens *et al.* 1989) and CH₄ (Ottosen
85 *et al.* 2009) emissions can be reduced by 70 - 90%. Thus, we fixed the value 5.5 as pH target below
86 which emission were expected to be decreased.

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

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



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

96 Sulfur was added to both co-digested and raw separated solid fractions at three rates: 0.5%, 1 % and
97 2% (w/w) calculated on wet basis (WB). Solid fraction after sulfur addition was thoroughly mixed
98 manually to evenly distribute the powdery product. Unacidified raw and co-digested solid fractions
99 were used as control. Prior to and after acidification, samples of all treatments were collected, and
100 stored at 4°C prior to chemical characterization. Dry matter (DM) content was measured after
101 drying (24h at 105 °C) the fresh samples to constant weight. The volatile solids content (VS) was
102 calculated as weight loss upon ignition at 550 °C for 5h (VDI 4630, 2006). Samples were weighted
103 using a four digits trusted balance (Kern®, mod. ABS 220-4). pH of the solid fractions prior and
104 during the experiment were measured by a glass electrode for semi solid-biomasses (Hanna
105 instruments® electrode HI 1053B). At the end of the trials pH was measured after solid fraction
106 dilution in deionized water, followed by 45 min of shaking, and then 15 min of settling (Jorgensen
107 & Jensen, 2009). Total N (N_{tot}) and total ammonia nitrogen (N-NH₃) were measured according to
108 the Kjeldahl standard method (AOAC, 1990).

109 *Measurement of gaseous emission*

110 Emission tests were performed by filling 2000cm³ jars with 1000cm³ of unacidified and acidified
111 solid fractions with three replicates per treatment. The bulk density of the tested raw and co-
112 digested solid fraction samples was estimated to be 500g/1000cm³. Gaseous (CO₂, CH₄, N₂O and
113 NH₃) emissions were measured by a ventilated chamber system and using an infrared photo
114 acoustic detector (IPD) (1412 Multi-gas Monitor, Innova® Air Tech Instruments, Ballerup,
115 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 CO₂-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 cm³/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 NH₃) 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 ($\alpha = 0.05$). Measured gaseous losses were converted into CO₂eq by using the IPCC (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.

156 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
157 temperature on the rate of S oxidations. Recorded temperatures were similar along the two
158 experiments. Average, minimum and maximum values are reported in Table 3.

160 NH_3 emissions

161 NH_3 emissions from raw-slurry separated solid fraction started to drop already at day 3 when pH
162 approached 5.5 (Fig. 2a). All treatments were effective, regardless of S application rate. Fig. 3
163 shows the total NH_3 emission quantified along the trial. The control (RS) lost as ammonia
164 approximately 6% of its initial total nitrogen content (Table 4). This value is consistent with that
165 (5.6%) measured by Dinuccio *et al.* (2008). Acidified samples lost 1.93% to 3.20% of their initial
166 total nitrogen (Table 4). Depending on the amount of added S, NH_3 emissions from RS 0.5, RS 1
167 and RS 2 acidified fractions were respectively 49%, 65% and 70% lower than those of the control
168 treatment. Specifically, the higher the S application rate, the higher the abatement efficacy. These
169 findings are consistent with measurement performed on raw slurry by Pain *et al.* (1990), Kai *et al.*
170 (2008) and Dai & Blanes-Vidal (2013) by using sulfuric acid as acidifying agent. The NH_3
171 emissions from co-digested solid fraction were twofold higher when compared to those of raw
172 separated solid fraction. This was probably due the higher initial N- NH_3 concentration (Table 1)
173 (Chadwick *et al.* 2011). All acidification treatments significantly reduced ammonia emissions by
174 approximately 65% with respect to untreated solid fraction. NH_3 emissions from acidified fractions
175 started to drop at day 7 (Fig. 2b), when pH approached 5.5 (Fig. 1b). The control (DS) lost on
176 average 19% of total initial nitrogen as ammonia, whereas from acidified solid fractions 6-7% of the
177 initial nitrogen was lost as ammonia (Table 4).

178 GHG emissions

179 The effect of S addition on GHG emissions from the storage of raw slurry and co-digested solid
180 fractions is displayed in Fig. 4. Although the two tests had different duration (30 and 60 days for
181 RSs and DSs respectively) total GHG emission from control samples (RS, DS) were in the range of
182 6 kg $\text{CO}_2\text{eq m}^{-2}$. N_2O was the most relevant GHG in both experiments. Acidification showed to be
183 more effective when applied on raw (non-digested) solid fractions. The highest emission reduction
184 (%) was obtained with 2% S addition, but this value was found to be not significantly ($p > 0.05$)
185 different from that (%) recorded for RS 1. A 0.5% S application rate was able to reduce by 44%
186 GHG emission when compared to control. The same S application rate (treatment DS 0.5) increased
187 $\text{CO}_2\text{eq.}$ emission by 44% when applied to co-digested solid fraction, due to high (+55%) N_2O
188 emissions. Nevertheless, DS 0.5 reached the target pH very late (after 30 days from S addition),
189 thus suggesting this rate to be too low for this kind of animal waste, being characterized by a high
190 initial pH and buffer capacity. N_2O emissions increasing were probably due to an enhanced
191 microbial activity with S as a growing factor (Sierra-Alvarez *et al.* 2007). Biogas obtained by
192 digesting pig slurry generally contains approximately 3000-8000 ppm hydrogen sulfide (H_2S) (Wei-
193 Chin Lin *et al.* 2012). Hydrogen sulfide have damaging effects on the engine components and
194 equipment and it is therefore removed before combustion in combined heat and power units. The
195 most common method for H_2S removal from biogas is based on the addition of a small amount of
196 oxygen or air (3-5% v/v) directly into the digester (Ramos & Fdz-Polanco, 2014). In this way it
197 takes place the biological aerobic oxidation of H_2S to elemental sulfur and sulphates by a

198 consortium of sulphur-oxidising microorganisms (e.g., Thiobacillus bacteria). This process can
199 results in the accumulation of elemental sulfur and sulphates in the digester. It is assumed that in
200 the co-digested slurry are present nitrifying prokaryotes that could have an affinity with sulfur.
201 Therefore a higher sulfur dose might be necessary to inhibit the nitrification/denitrification
202 biological activity of these bacteria that could be otherwise promoted by a lower S application rate.

203 Higher S application rates (DS 1 and DS 2) significantly reduced CO₂eq. losses (by 39% and 55%
204 respectively). With special regards to methane, by applying 2% sulfur a 54% losses reduction was
205 observed.

206 Conclusions

207 The addition of elemental S to solid fractions showed to be a reliable and effective method to
208 acidify raw and digested solid fractions. Thus, it can be considered as an alternative method to the
209 common sulfuric acid utilization. Sulfur addition led to significant reduction of gaseous losses (NH₃
210 and GHG) during the solid fractions storage. The most evident outcome is represented by the
211 significant reduction of NH₃ emissions rate for both the tested biomasses with abatement of up to
212 70% in raw slurry solid fraction and 65% for the digested one.

213 GHG emissions were respectively reduced from 44% to 78% according to the amount of S added to
214 non-digested solid fraction. The lower S rate significantly increased GHG emission from the
215 digested solid fraction only with special regards to increased N₂O losses.

216 The experimental results allow a first positive evaluation on the possibility to decrease the pH and
217 gaseous emissions by adding sulfur to solid manures, thus enabling an effective pollution reduction
218 without using strong acids. The latter aspect is indeed one of the main concerns and a major limit to
219 the diffusion of manure acidification at a European level.

220 According to our preliminary results 1% S might be considered as the best application rate,
221 allowing an emission reduction in line with the present acidification technology performances
222 (Fangueiro *et al.* 2014). However, according to the current market price of powdery sulfur for crop
223 protection purpose (1€/kg) the former application rate would cost around 5€ per ton of treated solid
224 fraction. This cost is five times higher than that of slurry acidification by H₂SO₄. Nevertheless, it
225 must be considered that besides the commercial powdery sulfur (normally used for crop protection),
226 sulfur is a byproduct of the oil refining process. The latter is considered as a waste and thus its reuse
227 in the animal waste management sector might considerably reduce the cost of slurry acidification.
228 Appropriate procedures for safely using a powdery acidifying product are already under study by
229 our research group. Moreover, the DISAFA-Waste Management Group is currently investigating
230 the feasibility to lower solid fraction pH by S addition to slurry prior to mechanical separation, with
231 the aim to i) reduce the S application rates and, ii) acidify both solid and liquid fractions with a
232 single treatment.

233

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334

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.

344

345

Table 1.

DM: dry matter, VS: volatile solids, N_{tot}: total nitrogen, N-NH₃: ammonia nitrogen

348

Table 2.

350

351

352

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

353

Table 4.

354

Trial	N_NH ₃ emitted (%N _{tot})
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

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357 Figures captions

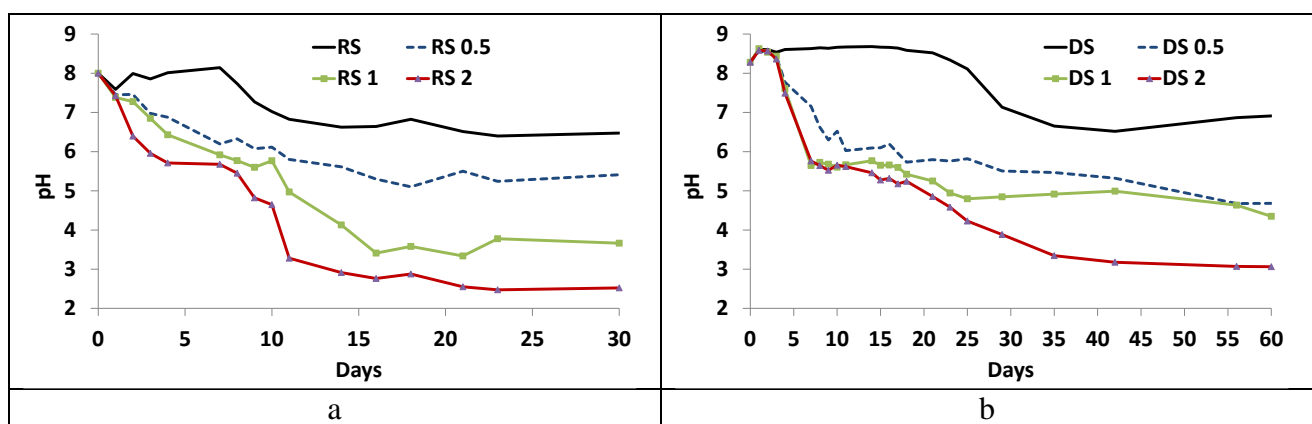
358 Fig. 1. Average pH values pattern of (a) raw slurry solid fraction and (b) co-digested solid fraction
359 samples along the experiment

360 Fig. 2. Emission fluxes of ammonia (NH₃) during storage of (a) raw slurry solid fraction and (b) co-
361 digested solid fraction. Error bars indicate standard deviation (number of observations=3)

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

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

366



367 Fig. 1.

368

369

370

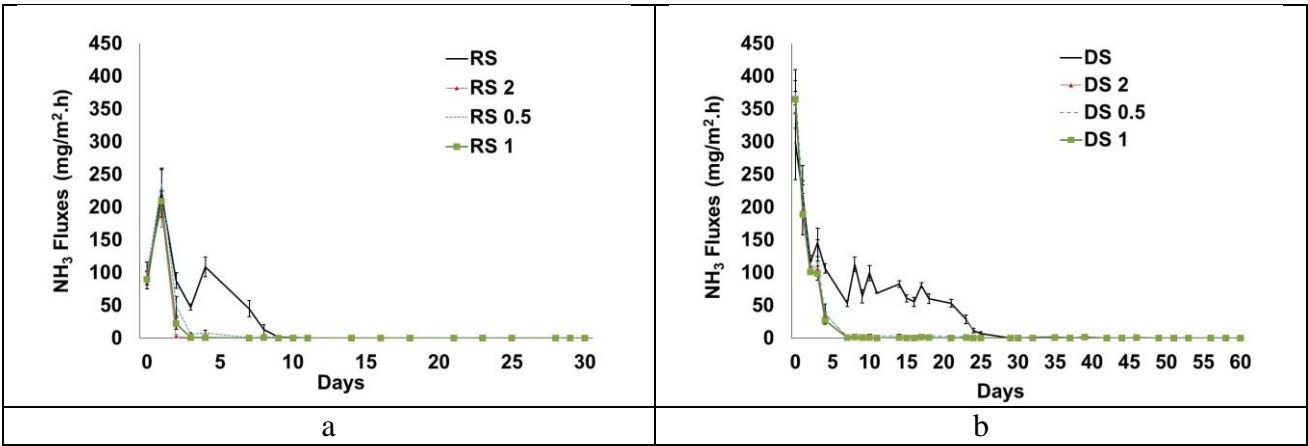


Fig. 2.

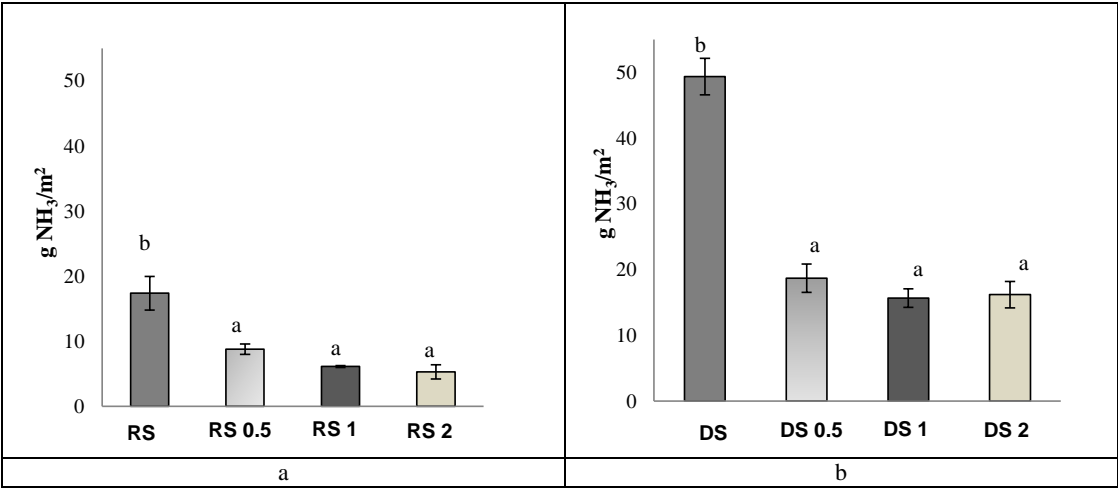


Figure 3.

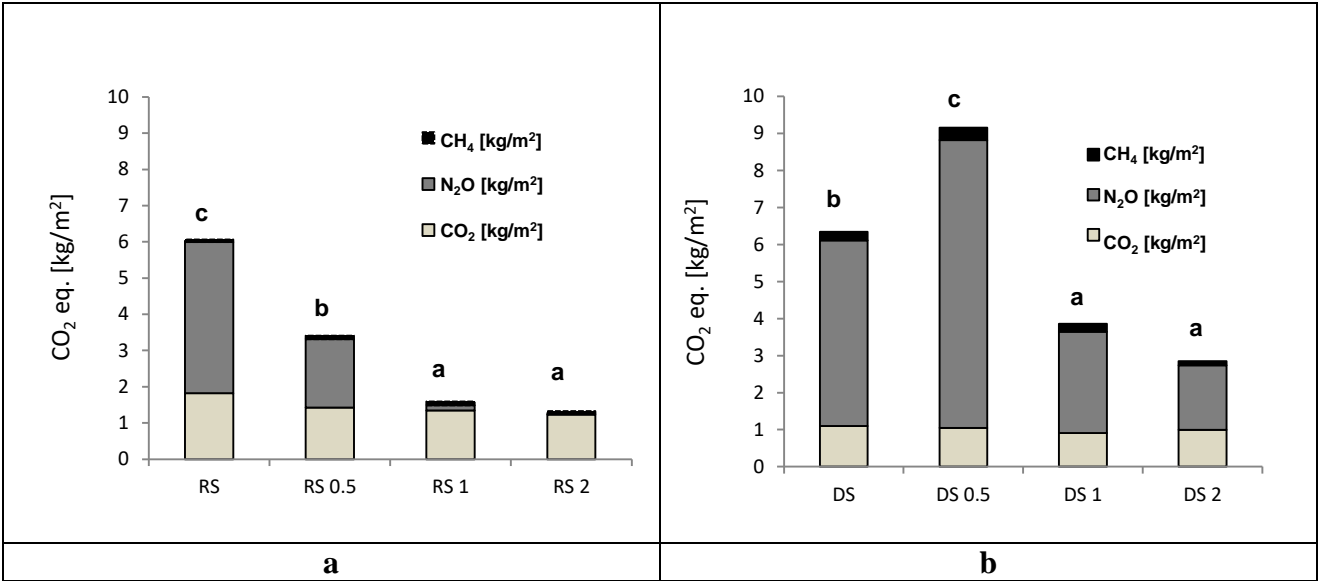


Fig. 4.