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Mitigating Ammonia and Greenhouse Gas Emissions from Stored Pig Slurry Using Chemical Additives and Biochars

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Abstract: Slurry storage is a significant source of NH_3 and greenhouse gas (GHG) emissions. The aim of this laboratory study was to assess the effects of different chemical additives and biochars on the emissions of NH_3, N_2O, CO_2, and CH_4 during the short-term storage of pig slurry. The experiment was performed using Kilner jars filled with raw slurry as control and six treatment additives (5% *w*/*w*): acidified slurry, alkalinized slurry, neutralized slurry, agroforestry biochar, cardoon biochar, and elderberry biochar. The gas emissions were measured for 30 days, and the composition of the slurries was determined. During short-term storage, the results of this laboratory study indicated that the NH_3 emissions were reduced by 58% by acidification and by 20% by the biochars (Agroforestry, Cardoon, and Elderberry treatments), while neutralization reduced this loss by only 12%. Nitrous oxide emissions were not reduced by the chemical additives (Acidified, Alkalinized, and Neutralized treatments), while this loss was increased by 12% by the biochars. Carbon dioxide, CH_4, and global warming potential emissions were not affected by the chemical additives and biochars. Furthermore, the absence of differences between the biochars may be related to their similar composition. Regarding the influence of the studied additives on NH_3 losses, it can be concluded that acidification was the best mitigation measure and the biochars were quite similar due to their composition. Furthermore, neutralization had the advantage of sanitizing the slurry, but only had a mild impact on NH_3 preservation.

Keywords: animal slurry; biochar; chemical additive; gaseous emissions; mitigation measure; slurry additive

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1. Introduction

The global animal supply chain represents 60% of the total ammonia (NH_3), 23% of the nitrogen oxide (NOx), and 32% of the nitrous oxide (N_2O) emissions of global human-induced nitrogen (N) emissions [1], representing about 33% of the total human-induced N emissions. Most N emissions are generated during feed production (e.g., following fertilizer N applications) and animal manure management, mainly via NH_3 volatilization, denitrification, and nitrate (NO_3^-) leaching [1]. Other greenhouse gas (GHG) emission from animal operations are methane (CH_4) from enteric fermentation and manure storage. At the EU-28 level, animal manure management is responsible for the majority of NH_3 emissions and one third of GHGs [2]. Emissions result from high animal densities, poor manure management, and/or poor disposal when these systems produce more manure than what can be recycled in the surrounding agricultural area. At the global scale, animal manure management generates ca. 40% of the anthropogenic NH_3 and N_2O emissions and 6% of the anthropogenic methane (CH_4) emissions [3]. The manure excreted in the EU-27 in 2010 was equivalent to 9.7 Tg N and its management contributed to 65% of the total anthropogenic NH_3, 40% of N_2O, and 10% of CH_4 emissions [3]. Most N losses from manure occurs via NH_3 volatilization, with losses representing between 30 and 70% of the ammonium (NH_4^+) content of manure [4,5].

Animal production, and more specifically, a lack of good manure management, is re-sponsible for a significant quantity of NH_3 and GHG emissions at a global scale. Several Best Available Techniques (BAT) are available to farmers to mitigate these losses and reduce the environmental impacts associated with animal manure management [6]. Gaseous emissions occur in all manure management stages—housing, storage, processing, and recycling as crop fertilizer after field application. Animal feeding strategies, such as reducing by 1% the crude protein, and feed supplements, such as clinoptilolite or Yucca extract, can be adopted to decrease NH_3 emissions. Regarding housing, floor designs such as double-sloped solid floor or grooved floors, management of cleanings by scraping or flushing, additives such as urease inhibitor, alum, or acidification, and treatment of exhaust air by scrubber or biofilters are the most efficient for lowering NH_3 emissions. At the storage level, covers by fixed lid or plastic cover, and additives such as acidification could be used to reduce NH_3 emissions. Regarding soil application, slurry application techniques, such as injection or acidification, are the most effective to reduce NH_3 emissions. However, it is important to consider potential pollution swapping when planning and implementing mitigation measures.

Emissions that occur during the storage of animal manure are the result of complex biological, physical, and chemical transformation processes [7]. Ammonium is in equilibrium with the NH_3 that will be lost by volatilization, leading also to carbon dioxide (CO_2) emissions [8]. During manure decomposition, N_2O and nitric oxide (NO) are emitted by the nitrification and denitrification processes [9]. Nitrification can be performed by autotrophic and heterotrophic organisms under aerobic conditions whereas denitrification is the stepwise reduction of NO_3^- to dinitrogen (N_2) under anaerobic conditions [10]. The availability of NH_4^+ and NO_3^- are the primary requirements for the nitrification and denitrification processes, respectively, but also the availability of easily degradable carbon (C) influences these processes [10]. Nitrous oxide emissions are quite low during liquid manure (slurry) storage due to the anaerobic conditions existing during slurry storage. However, the co-existence of aerobic and anaerobic conditions during solid manure storage or even close to the natural crust formed during liquid manure storage might stimulate both nitrification and denitrification, the main processes responsible for N_2O emissions [11]. The anaerobic decomposition of the organic matter by methanogenic bacteria leads to CH_4 and CO_2 emissions. Organic matter is considered a major limiting factor for CH_4 production, once anaerobiosis is established, and CH_4 emissions are closely related to manure temperature [12]. Management practices such as storage duration, agitation or mixing, and emptying of storage tanks play important roles in CH_4 emissions during storage [13]. Methane emissions during manure storage can represent up to 6.5 or 5.4 kg m^{-2} per year from covered and uncovered slurry pits, respectively [14].

A wide range of additives could be used at storage, where they act as acidifying and adsorbent additives, and can affect the microbial activity in slurries; they also have been shown to reduce slurry pH. Furthermore, biological additives constitute microbial strains and or enzymes, which facilitate biodegradation of organic materials in animal slurry. Previous studies proposed various strategies involving the amendment of additives to animal slurry in order to reduce NH_3 and GHG losses, namely, acidification (e.g., alum, sulfuric acid, and other dry acids) [15], bio-acidification (e.g., sugar sources, whey, and lactic acid) [16], urease and nitrification inhibitors (e.g., N-(n-butyl) thiophosphoric triamide (NBPT), 3,4-dimethylpyrazol phosphate (DMPP), and dicyandiamide (DCD)) [17,18], adsorbents (e.g., natural zeolites, agricultural gypsum, and biochars from agroforestry or manures) [8,19], and biological additives (e.g., Biobuster®, EU200®, and JASS®) [20]. There is the potential to use slurry additives to improve the handling properties, but a proper evaluation of the effects of slurry treatments is required to investigate the mode of action, as this information is often not disclosed by companies. An effective assessment of the effects of slurry treatments or the combination of different treatments in mitigating different emission processes should change from a single-stage approach to include real/pilot-scale experiments. These studies should be made using a slurry whole-life-cycle scale to avoid pollution swapping and simultaneously to determine the most efficient solution for manure energy and nutrients recovery.

The aim of this laboratory study was to assess the effects of different chemical additives and biochars on the emissions of NH_3, N_2O, CO_2, and CH_4 during the short-term storage of pig slurry.

2. Materials and Methods

2.1. Treatments

The raw slurry used in this study was collected in the outlet tube of a fattening pig building located in Viseu, Portugal, and the composition is given in Table 1. A laboratory experiment was conducted in which were considered the following seven treatments with three replications:

1. Raw slurry as control (treatment: Control);
2. Acidification of raw slurry to pH 5.0 (treatment: Acidified);
3. Alkalinization of raw slurry to pH 9.5 (treatment: Alkalinized);
4. Neutralization of raw slurry to pH 7.5 (treatment: Neutralized);
5. Raw slurry amended with wood shavings biochar (treatment: Agroforestry);
6. Raw slurry amended with cardoon biochar (treatment: Cardoon);
7. Raw slurry amended with elderberry biochar (treatment: Elderberry).

Table 1. Composition of the pig slurry and biochars used in the experiment ($n = 1$).

Parameter	**Raw Slurry**	**Agroforestry**	**Cardoon**	**Elderberry**	**Method**
pH (H_2O)	8.1	9.5	12.4	12.6	Potentiometry, EN 13037, Brussels, Belgium
Dry matter, g kg^{-1}	12.2	934.0	645.3	980.8	Gravimetric method, EN 13040, Brussels, Belgium
Total C, g kg^{-1}	41.2	759.0	448.0	670.0	Dumas method
Total N, g kg^{-1}	5.8	2.0	7.0	15.0	Kjeldahl method, EN 13654-1, Brussels, Belgium
NH_4^+-N, g kg^{-1}	3.4				Absorption spectrophotometry, EN 13652, Brussels, Belgium
NO_3^--N, mg kg^{-1}	1.7				Absorption spectrophotometry, EN 13652, Brussels, Belgium
Average particle size, µm		21	12	32	Sieving method
90% size of particles, µm		<37	<26	<59	Sieving method
Specific surface area, m^2 g^{-1}		22	180	32	Brunauer, Emmett, and Teller method
Pore volume, mm^3 g^{-1}		1.1	67.0	16.0	Mercury porosimetry

The treatment Control was obtained using a sample raw slurry (4000 g) without any additive, which was retained in closed plastic containers at 20 °C for 24 h.

The three treatments (Acidified, Alkalinized, and Neutralized) treated with chemical additives were obtained by the methodology described in Rodrigues et al. [21] and Pereira et al. [22]. The treatment Acidified was obtained using a sample of raw slurry (4000 g), which was acidified by adding 32 mL of concentrated H_2SO_4 (95% (*w*/*w*, Chem-Lab, Zedelgem, Belgium), to the target pH of 5.0. The treatment Alkalinized was obtained using a sample of raw slurry (4000 g), which was subjected to alkalinization with pH 9.5 that was achieved by adding 28 g of concentrated KOH (85% *w*/*w*, Macron Fine Chemicals, Radnor, PA, USA). The treatment Neutralized was obtained using a sample of raw slurry (4000 g), which was alkalinized to pH 9.5, and after 24 h, the slurry sample was neutralized to pH 7.5 by adding 16 mL of concentrated H_2SO_4 (95% *w*/*w*, AppliChem GmbH, Darmstadt, Germany).

The others three treatments (Agroforestry, Cardoon, and Elderberry) were amended with the biochars, each one at a rate of 50 g of additive per 1000 g of raw slurry, as recommended in previous studies [19,23]. The Agroforestry and Elderberry biochars were produced from wood shavings and stalks of cardoon (*Cynara cardunculus* L.), respectively, being pyrolyzed in a muffle furnace (900 °C); in turn, the Elderberry biochar was produced from stalks of elderberry (*Sambucus nigra* L.) and pyrolyzed in a muffle furnace at 550 °C. The main characteristics of the Agroforestry, Cardoon, and Elderberry biochars are presented in Table 1.

The samples of the treatments were subdivided into individual doses of 1 kg (three replications per treatment), and immediately stored in plastic containers and frozen (−18 °C) until required for the laboratory experiment. The subsamples were retained and analyzed by standard laboratory methods for the parameters reported in Table 2.

Table 2. Composition of the treatments at the beginning of the experiment (mean ± standard deviation) (n = 3).

Treatments	**pH**	**DM**	**TC**	**TN**	**NH_4^+**	**NO_3^-**	**NH_4^+/TN**	**C/N**
Control	8.1 ± 0.1 d	12.2 ± 0.3 ef	41.2 ± 2.9 a	5.8 ± 0.2 a	3.4 ± 0.1 cd	1.7 ± 0.5 a	0.6 ± 0.1 e	7.1 ± 0.5 a
Acidified	5.0 ± 0.1 f	13.8 ± 0.3 d	40.7 ± 1.7 a	5.8 ± 0.1 a	3.3 ± 0.1 d	0.8 ± 0.5 c	0.6 ± 0.1 e	7.0 ± 0.5 a
Alkalinized	9.5 ± 0.1 a	11.6 ± 0.4 f	39.6 ± 1.8 a	5.7 ± 0.2 a	3.4 ± 0.1 d	1.2 ± 0.5 b	0.6 ± 0.1 e	7.0 ± 0.5 a
Neutralized	7.5 ± 0.1 e	13.3 ± 0.7 de	37.4 ± 4.2 a	5.6 ± 0.3 a	3.8 ± 0.1 c	1.3 ± 0.5 b	0.7 ± 0.1 d	6.7 ± 0.5 a
Agroforestry	8.5 ± 0.1 c	58.9 ± 0.1 b	42.9 ± 2.8 a	5.5 ± 0.2 a	4.7 ± 0.1 b	1.7 ± 0.5 a	0.8 ± 0.1 b	7.7 ± 0.5 a
Cardoon	9.0 ± 0.1 b	62.9 ± 0.3 a	42.5 ± 2.7 a	5.6 ± 0.2 a	4.5 ± 0.1 b	1.7 ± 0.5 a	0.8 ± 0.1 c	7.5 ± 0.5 a
Elderberry	8.6 ± 0.1 c	43.8 ± 0.4 c	41.4 ± 2.8 a	5.6 ± 0.2 a	5.2 ± 0.2 a	1.8 ± 0.5 a	0.9 ± 0.1 a	7.4 ± 0.5 a

Note: n = 3: three replications per treatment. pH: pH (H_2O); Dry matter: DM (g kg^{-1}); Total C: TC (g kg^{-1}); Total N: TN (g kg^{-1}); NH_4^+: NH_4^+-N (g N kg^{-1}); NO_3^-: NO_3^-—N (mg N kg^{-1}); NH_4^+/TN: NH_4^+: total N ratio; C/N: C:N ratio. Values presented with different lowercase letters within columns are significantly different ($p < 0.05$), as per a Tukey test.

2.2. Measurement of Gaseous Emissions

For this, the experiment was run in a system of 12 Kilner jars (H = 23.0 cm, Ø = 10.5 cm, volume = 2 L) filled with 1000 g (H = 10.5 cm) of each treatment (in triplicate per treatment), under a constant temperature (20 ± 0.5 °C), airflow rate, and for 30 days [8,19]. Then, one air inlet and one air outlet were positioned symmetrically in the jar lid, inserting a Teflon tube (Ø = 3 mm) through one of the septa and the end kept 2 cm above the slurry surface. The airflow through the headspace of each jar was obtained by a pump (KNF, model N010.KN.18, Neuberger GmbH, Freiburg, Germany) with a 2.5 L min^{-1} flowrate controlled by a needle valve connected to a flow meter (Aalborg™ FT10201SAVN, Aalborg, Denmark). The inlet air passed through NH_3 trapping filters coated with $C_2H_2O_4$ and the outlet air of the Kilner jars was exhausted by a fume hood.

The gas concentrations (NH_3, N_2O, CO_2, and CH_4) were measured in the outlet air of the jars with a photoacoustic multigas monitor (INNOVA 1412i-5, Lumasense Technologies, Ballerup, Denmark) and air samples collected, in sequence (120 s intervals), through one sampling point (Ø = 3 mm) per Kilner jar, using a multipoint sampler (INNOVA 1409-12, Lumasense Technologies, Ballerup, Denmark) with polytetrafluoroethylene (PTFE) filters (1 µm pore size, Whatman, Ome, Japan). The photoacoustic monitor was equipped with an optical filter for water vapor (filter type SB0527, Lumasense Technologies, Ballerup, Denmark) and the detection limits for NH_3 (filter type UA0973, Lumasense Technologies, Ballerup, Denmark), N_2O (filter type UA0985, Lumasense Technologies, Ballerup, Denmark), CO_2 (filter type UA0982, Lumasense Technologies, Ballerup, Denmark), and CH_4 (filter type UA0969, Lumasense Technologies, Ballerup, Denmark) were, respectively, 152.1, 58.9, 2947.1, and 286.4 µg m^{-3}. The photoacoustic monitor was calibrated by the manufacturer before the starting of the experiment, being operated in a mode that compensated for water interference and cross interference.

The laboratory experiment was performed in triplicate and all treatments were included in each replication. Thus, seven sampling points of the multipoint sampler were used to measure the outlet gas concentrations of the seven treatments and the remaining sampling points were used to average the inlet gas concentrations.

2.3. Statistical Treatment of Data

The NH_3, N_2O, CO_2, and CH_4 concentrations were used to calculate the means per hour and day per each outlet an inlet sampling point. Thus, the emission of these four gases was determined (per hour) using a mass balance, as described in Equation (1):

$$\text{EMISSION} = \text{FLOWRATE} \times \left(\frac{\text{OUTLET} - \text{INLET}}{\text{AREA}}\right) \tag{1}$$

where EMISSION is the gas emission (mg m^{-2} h^{-1}), FLOWRATE is the air flowrate in the Kilner jar (m^3 h^{-1}), OUTLET is the outlet gas concentration (mg m^{-3}), INLET is the inlet gas concentration (mg m^{-3}), and AREA (m^2) is the emitting surface area of the Kilner jar.

The reduction efficiencies (REDUCTION, %) of the NH_3, N_2O, CO_2, and CH_4 emissions from the amended treatments, compared to the Control, were determined as described in Regueiro et al. [24], using Equation (2):

$$\text{REDUCTION} = 100 - ((\text{AMENDED}/\text{CONTROL}) \times 100) \tag{2}$$

where AMENDED is the mean value of the individual or cumulative gas values from the amended treatments, and CONTROL is the mean value of the individual or cumulative gas values from the Control.

The cumulative emissions of NH_3, N_2O, CO_2, and CH_4 were determined by averaging the flux between two sampling occasions and multiplying by the time interval between the measurements [8,19]. The cumulative emissions were expressed as the % total N or C applied in each amended treatment. The global warming potential (GWP) for each Kilner jar was assessed using the GWP coefficients for direct GHG emissions (265 for N_2O, 1 for CO_2, and 28 for CH_4) and indirect N_2O emissions (1% NH_3-N volatilized for N_2O-N) [8,25].

The data collected were analyzed by the statistical software package STATISTIX 10.0 (Analytical Software, Tallahassee, FL, USA). One-way analysis of variance (ANOVA) was used to test the effects of each treatment on the composition and gaseous emissions, and the statistical significance ($p < 0.05$) of the means' difference between treatments was determined by the Tukey's HSD (honestly significant difference) test.

3. Results and Discussion

3.1. Composition of the Slurries

The compositions of the treatments at the beginning (Day 0) of the experiment are presented in Table 2. The content of total C, total N, and the C/N ratio did not differ significantly ($p > 0.05$) between all treatments, with the values observed varying from 29 to 43 g kg^{-1} for total C, 5.5 to 5.8 g kg^{-1} for total N, and 6 to 8 for the C/N ratio (Table 2). The NH_4^+ content did not differ significantly ($p > 0.05$) among the Control and treatments with chemical additives (3.3 to 3.8 g kg^{-1}), being significantly higher ($p < 0.05$) in treatments with biochar (4.5 to 5.2 g kg^{-1}) (Table 2).

The slurry acidification reduces the NH_3 volatilization and preserves NH_4^+ because it lowers its pH from 3.5 to 5.5 and modifies the NH_4^+/NH_3 ratio to 98.00–99.98% NH_4^+ [15]. The slurry alkalinization reduces the number of pathogens and increases the NH_3 volatilization by raising its pH from 9.0 to 11.0 [21,22]. Thus, the use of alkalinized slurry is a safer solution than raw slurry regarding the risk of groundwater pollution [26]. The slurry neutralization reduces the risks pointed for slurry alkalinization by lowering the pH from 9.5 to 7.5 [21,22]. In this study, for most parameters, the composition of the treatments with chemical additives and raw slurry did not differ significantly (Table 2), although some contradictions have been reported in previous studies: Regueiro et al. [24] observed higher concentrations of total solids in acidified pig slurry relative to raw slurry whereas Pereira et al. [22] recorded higher concentrations of DM and TC in raw slurry.

Previous studies reported that the biochar properties are highly dependent on the temperature (300–1000 °C), time of pyrolysis, final acidity, and feedstock from which the biochar is produced [27]. Compared to raw slurry, the addition of biochar to the slurry increases the pH value, C/N ratio, cation-exchange capacity, and microbial activities [28–32], in line with this study in which an increase in DM and NH_4^+ was observed in treatments with biochar. Although the specific surface area and porosity were higher in Cardoon than Agroforestry or Elderberry, an absence of differences in the composition of treatments with biochar added to slurry was observed, which could be related to the solution pH in these treatments being similar (Table 2).

3.2. Nitrogen Emissions

As can be observed in Table 3, the daily NH_3 fluxes peaked on Day 1 and decreased in all treatments until the end of the experiment (from 6789 to 82 mg m^{-2} h^{-1}). The NH_3 fluxes did not differ significantly ($p > 0.05$) between the Control and Neutralized treatments during the experiment; however, the Acidified treatment significantly reduced ($p < 0.05$) these fluxes by 64% in the first 20 days while the Alkalinized treatment significantly increased ($p < 0.05$) by 409% in the first 4 days (Table 3). Compared to the Control treatment, the NH_3 fluxes from the biochar treatments (Agroforestry, Cardoon, and Elderberry) decreased by 45% in the first 6 days and 18% in the 30 days of the experiment, although this reduction was not statistically significant ($p > 0.05$) (Table 3). The cumulative emissions of NH_3, expressed in g m^{-2} or as % of total N applied, did not differ significantly ($p > 0.05$) between the Control, Neutralized, and biochar treatments; nevertheless, 12 and 20% reductions were observed in the Neutralized and biochar treatments, respectively (Tables 3 and 4). Compared to all other treatments, the cumulative emissions of NH_3, expressed in g m^{-2} or as % of total N applied, of the Acidified treatment decreased significantly ($p < 0.05$) by 58%, while these same losses were increased significantly ($p < 0.05$) by 114% in the Alkalinized treatment (Tables 3 and 4).

As can be observed in Table 4, the NH_3 emissions decreased by 58% through the maintenance of a low and stable pH by the addition of sulfuric acid, whereas these losses were reduced by 20% due to adsorption of NH_4^+ by the addition of biochar. Thus, the slurry acidification was efficient in preserving the NH_3 because the amount of NH_4^+ and NH_3 that was dissociated as NH_3 gas is about 6/1000 at pH = 5.0 and temperature = 25 °C [33]. The results of this study are in the same range to those reported in previous studies [15,34], where the acidification of pig slurry reduced NH_3 emissions from 50 to 88% relative to raw slurry; they also found that the slurry alkalinization enhances NH_3 losses, particularly in the first days of storage, while the slurry neutralization decreases NH_3 losses below the baseline of the raw slurry, corroborating Pereira et al. [22]. On other hand, the enhancement of the NH_4^+ and NH_3 binding by the high specific surface area and cation exchange capacity of the biochars led to a decrease in NH_3 losses [28]. The results revealed that the addition of a biochar reduced the NH_3 emissions, which agreed with previous studies [8,19,30] who added biochar (1–12% *w*/*w*) to animal manure, reducing the NH_3 emissions from 12 to 77%.

Table 3. Mean values of daily (mg m^{-2} h^{-1}) and total (mg m^{-2}) ammonia fluxes observed in the treatments (mean ± standard deviation) (n = 3).

Treatments	**Days of Experiment**										**Total Flux**
	1	**2**	**3–4**	**5–6**	**7–8**	**9–11**	**12–15**	**16–20**	**21–25**	**26–30**	**∑0–30**
Control	806 ± 15 bc	849 ± 25 bc	678 ± 25 b	501 ± 16 a	361 ± 12 a	380 ± 16 ab	346 ± 15 a	242 ± 1 ab	137 ± 1 b	110 ± 3 b	256,397 ± 5725 b
Acidified	203 ± 5 c	214 ± 10 d	193 ± 11 c	168 ± 9 b	145 ± 8 b	147 ± 9 c	149 ± 8 c	127 ± 3 cd	112 ± 3 b	106 ± 1 bc	107,638 ± 3624 c
Alkalinized	6789 ± 229 a	3851 ± 197 a	1575 ± 168 a	563 ± 89 a	248 ± 31 ab	155 ± 10 c	129 ± 3 c	110 ± 1 d	99 ± 1 b	93 ± 1 cd	538,707 ± 27,004 a
Neutralized	1182 ± 90 b	959 ± 67 b	585 ± 50 bc	378 ± 44 ab	253 ± 31 ab	227 ± 31 bc	211 ± 28 bc	177 ± 25 bcd	132 ± 25 b	102 ± 14 bc	221,383 ± 21,434 b
Agroforestry	335 ± 44 c	345 ± 25 cd	363 ± 33 bc	325 ± 22 ab	305 ± 20 ab	322 ± 28 ab	261 ± 25 ab	240 ± 30 ab	119 ± 30 b	82 ± 8 d	178,492 ± 15,357 bc
Cardoon	444 ± 18 c	392 ± 15 cd	396 ± 17 bc	341 ± 14 ab	324 ± 12 a	353 ± 14 ab	297 ± 12 ab	338 ± 19 a	228 ± 19 a	165 ± 8 a	228,547 ± 8836 b
Elderberry	345 ± 47 c	359 ± 39 cd	407 ± 49 bc	405 ± 50 ab	404 ± 50 a	390 ± 44 a	266 ± 22 ab	232 ± 18 abc	139 ± 18 b	111 ± 1 b	200,799 ± 17,796 bc

Note: n = 3: three replications per treatment. For each gas, values presented with different lowercase letters within columns are significantly different ($p < 0.05$), as per a Tukey test.

Table 4. Cumulative nitrogen and carbon losses observed in the treatments (mean ± standard deviation) (n = 3).

Treatments	**NH$_3$ (% Total N Applied)**	**N$_2$O (% Total N Applied)**	**N (g m^{-2})**	**N (% Total N Applied)**	**CO$_2$ (% Total C Applied)**	**CH$_4$ (% Total C Applied)**	**C (g m^{-2})**	**C (% Total C Applied)**	**GWP (g CO$_2$-eq. m^{-2})**
Control	31.4 ± 0.5 b	0.7 ± 0.1 d	215.9 ± 8.2 b	32.1 ± 0.5 b	78.0 ± 5.0 a	1.7 ± 0.2 a	3799.5 ± 43.0 abc	79.7 ± 5.2 a	19,008.6 ± 10.0 abc
Acidified	13.3 ± 0.9 c	0.7 ± 0.1 d	93.4 ± 10.1 c	14.0 ± 0.9 c	75.8 ± 3.7 a	1.6 ± 0.1 a	3637.0 ± 83.7 cd	77.4 ± 3.8 a	18,198.6 ± 316.9 c
Alkalinized	68.0 ± 6.9 a	0.7 ± 0.1 bcd	448.4 ± 77.1a	68.4 ± 6.9 a	77.4 ± 3.3 a	1.8 ± 0.1 a	3625.2 ± 17.5 d	79.3 ± 3.4 a	18,525.2 ± 86.6 bc
Neutralized	27.8 ± 4.3 b	0.7 ± 0.1 cd	187.0 ± 61.3 b	28.7 ± 4.3 b	84.8 ± 11.8 a	1.8 ± 0.3 a	3743.4 ± 119.9 bcd	86.6 ± 12.0 a	18,603.8 ± 311.2 bc
Agroforestry	22.8 ± 3.0 bc	0.8 ± 0.1 abc	152.1 ± 44.1 bc	23.7 ± 3.0 bc	75.3 ± 4.0 a	1.6 ± 0.1 a	3811.6 ± 156.7 ab	76.9 ± 4.1 a	19,125.5 ± 466.5 abc
Cardoon	29.2 ± 2.7 b	0.8 ± 0.1 a	193.5 ± 25.3 b	29.8 ± 2.7 b	78.6 ± 5.3 a	1.7 ± 0.1 a	3942.4 ± 83.7 a	80.3 ± 5.5 a	19,880.7 ± 217.7 a
Elderberry	25.5 ± 3.5 bc	0.8 ± 0.1 ab	170.5 ± 51.1 bc	26.5 ± 3.5 bc	78.3 ± 4.1 a	1.7 ± 0.1 a	3829.5 ± 187.8 ab	80.0 ± 4.2 a	19277.9 ± 587.4 ab

Note: n = 3: three replications per treatment. Values presented with different lowercase letters within columns are significantly different ($p < 0.05$), as per a Tukey test. N: $NH_3 + N_2O$; C: $CO_2 + CH_4$; GWP: global warming potential expressed in CO_2 equivalents (CO_2 = 1, CH_4 = 28, direct N_2O = 265, and indirect N_2O = 1% NH_3-N volatilized).

As can be seen in Table 5, no major variations were observed between treatments in the daily N_2O fluxes throughout the 30 days of the experiment (8 to 12 mg m^{-2} h^{-1}), with higher fluxes in the treatments with biochars. The daily N_2O fluxes from the Control and treatments with chemical additives (Acidified, Alkalinized, and Neutralized) did not differ significantly ($p > 0.05$), with the exception of the first 2 days, were the fluxes decreased significantly ($p < 0.05$) by 19% in the Alkalinized treatment (Table 5). The N_2O fluxes from the biochar treatments were significantly higher ($p < 0.05$) than most measurements after the first 15 days when compared with the Control treatment, followed by an absence of significant differences ($p > 0.05$) among all treatments at the end of the experiment (Table 5). The cumulative N_2O emissions, expressed in g m^{-2} or as a % of total N applied, were not significantly different ($p > 0.05$) among the Control and treatments with chemical additives, whereas the fluxes of these treatments were significantly lower ($p < 0.05$), by 12%, when compared with the biochar treatments (Tables 4 and 5).

Nitrous oxide losses were shown to arise from the nitrification and denitrification processes due to the presence of aerobic and anaerobic conditions in the stored slurries and under a dry crust that has formed on the surface [35]. The reduction in N_2O emissions by acidification is usually related to the inhibition of the nitrification/denitrification processes, but some contradictions are observed in previous studies. For example, Kupper et al. [34] reported that the pig slurry acidified with sulfuric acid increased the N_2O loss by 39%, while Pereira et al. [8] found that raw pig slurry or their derived liquid fraction amended with alum (5% *w*/*w*) had no significant effect on N_2O reduction. The decrease in N_2O emissions by biochar is related to the adsorption of NH_4^+, which could reduce its availability for nitrification. In this study, the higher N_2O emissions from the biochar treatments originated from anaerobic and aerobic microsites that occurred in the samples, being related to the higher amounts of DM observed in these treatments (Table 2), water evaporation, and dry conditions, together with air-filled porosity [36]. However, Pereira et al. [8] reported that raw pig slurry or its derived liquid fraction amended with biochar (5% *w*/*w*) had no significant effect on N_2O reduction, which may be related to the previously stated.

The cumulative N (NH_3 + N_2O) emissions, expressed in g m^{-2} or as % of total N applied, were not significantly different ($p > 0.05$) between the Control, Neutralized, and biochar treatments; furthermore, a decrease in the Neutralized and biochar treatments of 12 and 19% was observed, respectively (Table 4). The cumulative N (NH_3 + N_2O) emissions, expressed as g m^{-2} or as % of applied N, were reduced significantly ($p < 0.05$), by 57%, in the Acidified treatment, and increased significantly ($p < 0.05$), by 110%, in the Alkalinized treatment, when compared to all other treatments (Table 4).

3.3. Carbon Emissions

As can be seen in Table 6, in the 30 days of the experiment, small variations were observed between the daily CO_2 fluxes of all treatments (17 to 22 g m^{-2} h^{-1}), with numerically higher fluxes in most measurement dates of the treatments with biochars. The daily fluxes of CO_2 from the Control and treatments with chemical additives (Acidified, Alkalinized, and Neutralized) were not significantly different ($p > 0.05$), except between Days 2 and 15, where fluxes decreased significantly ($p < 0.05$) by 10% in the Acidified and Alkalinized treatments (Table 6). The CO_2 fluxes from the Control and biochar treatments did not differ significantly ($p > 0.05$) at almost all measurement dates (Table 6). The cumulative CO_2 emissions, expressed in g m^{-2} or as % of total C applied, were not significantly different ($p > 0.05$) among all treatments, with CO_2 losses that ranged from 75 to 85% of total C applied (Tables 4 and 6).

Table 5. Mean values of daily (mg m^{-2} h^{-1}) and total (mg m^{-2}) nitrous oxide fluxes observed in the treatments (mean ± standard deviation) (n = 3).

Treatments	**Days of Experiment**										**Total Flux**
	1	**2**	**3–4**	**5–6**	**7–8**	**9–11**	**12–15**	**16–20**	**21–25**	**26–30**	**∑0–30**
Control	11 ± 1 bc	10 ± 1 b	9 ± 1 b	10 ± 1 c	10 ± 1 c	9 ± 1 b	9 ± 1 b	11 ± 1 ab	10 ± 1 b	9 ± 1 b	7399 ± 39 c
Acidified	10 ± 1 c	10 ± 1 b	10 ± 1 b	10 ± 1 c	10 ± 1 bc	10 ± 1 b	9 ± 1 b	10 ± 1 b	10 ± 1 ab	10 ± 1 ab	7492 ± 113 bc
Alkalinized	8 ± 1 d	8 ± 1 c	9 ± 1 b	10 ± 1 c	10 ± 1 bc	10 ± 1 b	9 ± 1 b	11 ± 1 ab	11 ± 1 a	10 ± 1 a	7527 ± 20 bc
Neutralized	10 ± 1 c	9 ± 1 b	9 ± 1 b	9 ± 1 c	10 ± 1 c	9 ± 1 b	9 ± 1 b	10 ± 1 b	10 ± 1 ab	10 ± 1 ab	7419 ± 69 c
Agroforestry	11 ± 1 ab	11 ± 1 a	11 ± 1 a	10 ± 1 b	10 ± 1 abc	11 ± 1 a	11 ± 1 a	11 ± 1 ab	10 ± 1 b	10 ± 1 ab	7946 ± 115ab
Cardoon	12 ± 1 a	12 ± 1 a	11 ± 1 a	11 ± 1 a	11 ± 1 a	11 ± 1 a	11 ± 1 a	11 ± 1 a	10 ± 1 ab	10 ± 1 a	8238 ± 45 a
Elderberry	11 ± 1 a	11 ± 1 a	11 ± 1 a	10 ± 1 ab	10 ± 1 ab	11 ± 1 a	11 ± 1 a	11 ± 1 ab	10 ± 1 ab	10 ± 1 ab	8068 ± 161 a

Note: n = 3: three replications per treatment. For each gas, values presented with different lowercase letters within columns are significantly different ($p < 0.05$), as per a Tukey test.

Table 6. Mean values of daily (g m^{-2} h^{-1}) and total (g m^{-2}) carbon dioxide fluxes observed in the treatments (mean ± standard deviation) (n = 3).

Treatments	**Days of Experiment**										**Total Flux**
	1	**2**	**3–4**	**5–6**	**7–8**	**9–11**	**12–15**	**16–20**	**21–25**	**26–30**	**∑0–30**
Control	19.0 ± 0.2 abc	19.6 ± 0.2 a	19.0 ± 0.2 a	18.1 ± 0.1 a	17.0 ± 0.1 b	17.4 ± 0.1 b	17.6 ± 0.1 a	18.8 ± 0.1 ab	17.6 ± 0.1 bc	17.4 ± 0.1 b	13,633.7 ± 50.1 abc
Acidified	21.8 ± 1.6 a	16.4 ± 0.1 d	16.6 ± 0.1 b	16.5 ± 0.1 b	15.8 ± 0.1 c	16.1 ± 0.1 c	16.5 ± 0.1 b	18.0 ± 0.1 ab	17.5 ± 0.1 bc	17.5 ± 0.1 b	13,060.6 ± 82.7 cd
Alkalinized	16.3 ± 0.1 c	16.2 ± 0.1 d	16.5 ± 0.1 b	16.4 ± 0.1 b	15.9 ± 0.1 c	16.3 ± 0.1 bc	16.7 ± 0.1 b	18.2 ± 0.1 ab	17.8 ± 0.1 abc	17.7 ± 0.1 ab	12,983.3 ± 16.0 d
Neutralized	17.2 ± 0.2 bc	17.4 ± 0.3 c	18.1 ± 0.4 a	17.7 ± 0.3 a	16.7 ± 0.2 bc	16.8 ± 0.2 bc	17.2 ± 0.2 ab	19.0 ± 0.1 a	18.0 ± 0.1 ab	17.6 ± 0.1 ab	13,447.4 ± 123.6 bcd
Agroforestry	19.1 ± 0.4 abc	18.2 ± 0.3 bc	18.4 ± 0.3 a	17.7 ± 0.2 a	18.4 ± 0.2 a	19.6 ± 0.3 a	17.6 ± 0.2 a	18.0 ± 0.3 ab	17.5 ± 0.1 c	17.4 ± 0.1 b	13,685.0 ± 158.9 ab
Cardoon	19.8 ± 0.2 ab	18.8 ± 0.1 ab	19.0 ± 0.1 a	18.2 ± 0.1 a	18.8 ± 0.1 a	20.2 ± 0.1 a	18.0 ± 0.1 a	18.8 ± 0.2 ab	18.3 ± 0.1 a	17.9 ± 0.1 a	14,145.5 ± 86.2 a
Elderberry	18.8 ± 0.3 abc	18.4 ± 0.3 bc	18.7 ± 0.4 a	18.3 ± 0.4 a	19.0 ± 0.4 a	19.8 ± 0.4 a	17.6 ± 0.2 a	17.9 ± 0.3 b	17.4 ± 0.1 c	17.4 ± 0.1 b	13,745.3 ± 189.5 ab

Note: n = 3: three replications per treatment. For each gas, values presented with different lowercase letters within columns are significantly different ($p < 0.05$), as per a Tukey test.

The CO_2 emissions come from the microbial degradation of the organic matter and hydrolysis of urea [37], being related to the release of the CO_2 dissolved in the slurry itself and/or bicarbonate and carbonate present in the slurries at storage. Typically, the CO_2 losses from the acidification process occur at rates 2–10 times higher than during the subsequent storage [15]. In this study, the decrease in CO_2 fluxes between Days 2 and 15 and the absence of differences among the Control and treatments with chemical additives after the 30 days of storage (Tables 4 and 6) are in line with Fangueiro et al. [38], who observed lower CO_2 emissions from acidified than from raw slurry over the whole storage period, and Dai and Blanes-Vidal [39] who did not find significant differences over 40 days of storage. Previous studies reported that the addition of biochar (2.5–5.0% *w*/*w*) to pig slurry led to a decrease in CO_2 losses of 25–50% [8,19], by either sorption onto the biochar or a reduction in the labile C availability, being affected by differences among the biochars, such as the feedstock, method, and temperature pyrolysis. However, the results of this study revealed an absence of a significant effect on CO_2 reduction, although Czekała et al. [40] reported that CO_2 emissions from animal manure increased by between 7 and 8% through the addition of biochar (5–10% *w*/*w*).

As can be seen in Table 7, the daily fluxes in CH_4 followed the same trend in the treatments, with a progressive increase (86 to 228 mg m^{-2} h^{-1}) throughout the 30 days of the experiment, except for the Alkalinized treatment, which had a progressive decrease (266 to 99 mg m^{-2} h^{-1}) from the beginning until the end of the experiment (Table 7). Compared to the Control and Neutralized treatments, the daily CH_4 fluxes were significantly higher ($p < 0.05$), by 87%, for the Alkalinized treatment, and significantly lower ($p < 0.05$), by 20%, for the Acidified treatment in the first 2 days of the experiment. From to this day until the end of the experiment, there were no significant differences ($p > 0.05$) between the daily CH_4 fluxes of these treatments (Table 7). The daily CH_4 fluxes did not differ significantly ($p > 0.05$) among the biochar treatments, being significantly higher ($p < 0.05$), by 17%, than the Control treatment in the first 11 days of the experiment (Table 7). The cumulative CH_4 emissions, expressed in g m^{-2} or as a % of total C applied, were not significantly different ($p > 0.05$) between all treatments, with CH_4 losses that ranged from 1.6 to 1.8% of total C applied (Tables 4 and 7).

Methane emissions can originate through the degradation of organic matter under anaerobic conditions during slurry storage [41] The results of this study (20% CH_4 reduction for treatment Acidified in the first 2 days) are lower than other published studies [15,42], who reported a 67–87% reduction with sulfuric acid acidification. This result may be related to the fact that CH_4 emissions should be reduced by long-term acidification treatments, but not by short-term acidification, and considering that CO_2 emissions occurred mainly under aerobic conditions, no significant CH_4 emissions were expected [8,15]. Additionally, the low depth (H = 10.5 cm) of the slurry and the high airflow rate (2.5 L min^{-1}) in jars may have led to aerobic conditions in this study. On the other hand, in the 2 first days of storage, the slurry alkalinization increased the CH_4 emissions by 87% because the gas loss increased with pH [43]. Biochar reduces CH_4 emissions due to its adsorption capacity [28], but no differences were found between the three biochars evaluated in this study, which may be related to the similarity in its composition (Table 2). However, although the specific surface area and porosity were higher in Cardoon than in Agroforestry or Elderberry, this experiment did not reveal significant differences among CH_4 or other gas losses from the three biochars (Tables 1–7). The results of this study show lower values than those in previous studies [8,19], which found that CH_4 emissions from pig slurry were reduced by between 50 and 55% by the addition of biochar (2.5–5.0% *w*/*w*). This lack of a significant effect on CH_4 losses may be related to the same reasons previously indicated for CO_2 losses.

The cumulative C (CO_2 + CH_4) emissions (expressed in g m^{-2} or as % of total C applied) and the cumulative GWP emissions (expressed as CO_2 eq. m^{-2}) were not significantly different ($p > 0.05$) between all treatments, although numerically lower values were observed in treatments with chemical additives and higher values in treatments with biochars (Table 4).

Table 7. Mean values of daily (mg m^{-2} h^{-1}) and total (mg m^{-2}) methane fluxes observed in the treatments (mean ± standard deviation) (n = 3).

Treatments	**Days of Experiment**										**Total Flux**
	1	**2**	**3–4**	**5–6**	**7–8**	**9–11**	**12–15**	**16–20**	**21–25**	**26–30**	**∑0–30**
Control	112 ± 1 c	164 ± 2 bc	164 ± 1 bc	153 ± 1 b	226 ± 24 a	129 ± 1 b	159 ± 1 a	171 ± 9 a	137 ± 1 b	173 ± 1 b	121,827 ± 1924 ab
Acidified	86 ± 4 c	136 ± 4 d	146 ± 3 c	141 ± 3 b	148 ± 1 b	122 ± 2 b	153 ± 3 ab	142 ± 4 ab	112 ± 5 ab	190 ± 6 a	112,559 ± 2640 b
Alkalinized	266 ± 7 a	227 ± 6 a	177 ± 5 ab	148 ± 2 b	152 ± 1 b	124 ± 1 b	156 ± 1 a	149 ± 1 ab	99 ± 1 ab	198 ± 1 a	126,449 ± 1023 ab
Neutralized	109 ± 4 c	143 ± 4 cd	148 ± 3 c	141 ± 2 b	159 ± 3 b	120 ± 1 b	152 ± 2 ab	148 ± 1 ab	132 ± 1 ab	186 ± 2 ab	113,846 ± 1391 ab
Agroforestry	156 ± 6 b	183 ± 6 b	184 ± 7 ab	181 ± 4 a	192 ± 3 ab	199 ± 4 a	140 ± 2 c	128 ± 5 b	119 ± 3 ab	140 ± 2 c	119,022 ± 2860 ab
Cardoon	167 ± 2 b	190 ± 2 b	197 ± 2 a	193 ± 1 a	201 ± 1 ab	211 ± 1 a	146 ± 1 bc	140 ± 2 b	228 ± 1 a	148 ± 1 c	126,765 ± 985 a
Elderberry	154 ± 6 b	178 ± 6 b	187 ± 8 ab	190 ± 6 a	199 ± 6 ab	205 ± 7 a	142 ± 3 c	130 ± 5 b	139 ± 4 ab	142 ± 3 c	121,144 ± 3843 ab

Note: n = 3: three replications per treatment. For each gas, values presented with different lowercase letters within columns are significantly different ($p < 0.05$), as per the Tukey test.

4. Conclusions

During short-term storage, the results of this laboratory study indicated that the NH_3 emissions were reduced by 58% by acidification and by 20% by biochars (Agroforestry, Cardoon, and Elderberry), while neutralization reduced this loss by only 12%. Nitrous oxide emissions were not reduced by chemical additives (Acidified, Alkalinized, and Neutralized), while this loss was reduced by 12% by the biochars. Carbon dioxide, CH_4, and GWP emissions were not affected by the chemical additives and biochars. Furthermore, the absence of differences between the biochars may be related to their similar composition. Regarding the influence of the studied additives on NH_3 losses, it can be concluded that acidification was the best mitigation measure and the biochars were quite similar due to their composition. Furthermore, neutralization had the advantage of sanitizing the slurry, but had a mild impact on NH_3 preservation. More studies are needed under real storage conditions, evaluating isolated or combined additives, and considering all stages of slurry management to avoid pollution swapping.

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