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Optimizing Livestock By-Products Storage to Reduce Ammonia and Greenhouse Gas Emissions Using Biochar and Wood Vinegar

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Abstract: The environmental impact of livestock by-products presents significant challenges, particularly in regions with intensive farming and high pollution levels, such as the Po Valley. This study evaluated the effectiveness of biochar and wood vinegar in reducing gaseous emissions during the laboratory-scale storage of livestock slurry, digestate, and liquid fractions. Various types and applications of biochar, both with and without wood vinegar, were tested across three independent incubation periods of varying durations. The results showed that ammonia (NH_3) emissions were lower from slurry compared to raw digestate and the liquid fraction, while methane (CH_4) emissions exhibited the opposite trend. Pyrolysis biochar effectively reduced NH_3 emissions by 47% on average when applied as a 5 cm surface layer. However, its effectiveness was inconsistent when mixed into the material or when produced via gasification. Biochar activated with wood vinegar significantly reduced NH_3 emissions from both slurry and digestate by 61%, but it also led to increased emissions of CH_4 and CO_2. Nitrous oxide (N_2O) emissions were detected only after at least one month of incubation and were higher when biochar was used as a cover alone or when activated with wood vinegar. Overall, applying biochar as a cover and activating it with wood vinegar proved effective in reducing NH_3 emissions during the storage of livestock by-products. However, the effectiveness varied significantly depending on the type of biochar and its method of application, particularly with respect to CH_4 emissions, highlighting the need for careful consideration when using wood vinegar-activated biochar.

Keywords: NH_3 emissions; greenhouse gases; biochar; wood vinegar; slurry; digestate

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1. Introduction

The livestock sector plays an important role in climate change, contributing 14.5% to all human-induced greenhouse gas (GHG) emissions, of which livestock waste storage and processing represent 10% [1]. The largest percentage (44%) is represented by methane (CH_4) produced by enteric fermentation, whereas manure management is responsible for 5.7% and 4.3% of global livestock CH_4 and nitrous oxide (N_2O) emissions, respectively [2]. Additional nitrogen (N) losses occur through ammonia (NH_3) emissions, which significantly harm human health and ecosystems by contributing to eutrophication, acidification, and fine particulate matter ($PM_{2.5}$) formation. In Europe, 94% of NH_3 emissions originate from agriculture, with livestock farming accounting for 87% of these emissions [3,4]. Manure

management in the Po Valley faces distinct challenges due to high livestock density and intensive agriculture, which significantly impact air and water quality [5]. The Po Valley is highly vulnerable to nitrate leaching due to intensive agriculture and livestock density. To comply with the EU Nitrates Directive (91/676/EEC), regulations limit N application to 170 kg N/hectare in nitrate vulnerable zones (NVZs), promoting technologies like anaerobic digestion and combustion to manage manure efficiently [6].

On the other hand, livestock wastes are valuable sources of nutrients and organic matter (OM) that help maintain soil fertility and support crop production [7]. They provide readily available nutrients to crops, improve soil physical properties, stimulate soil biological activity by supplying easily degradable carbon (C) compounds, and contribute to the buildup of soil OM [8,9]. Their potential use as alternatives to mineral fertilizers presents new opportunities within a circular economy framework [10].

Currently, several techniques to mitigate emissions and preserve N during manure storage are available, including anaerobic digestion [11], composting [10], solid–liquid separation [12], and manure covers [13].

The environmental impact of these techniques is not straightforward, as gaseous emissions result from biological processes that occur under varying conditions. Effective mitigation of N losses in one form (e.g., NH_3) is often offset by increased losses in other forms (e.g., nitrite, N_2O, or nitrate). Similarly, reductions in CH_4 emissions achieved through solid–liquid separation or aeration may lead to increased CO_2 emissions or N losses [14]. Therefore, the interactive effects of different mitigation strategies on overall GHG and NH_3 emissions from livestock waste must be carefully considered.

Biochar addition is a promising technique to reduce emissions from manure during storage. Studies have shown that biochar can reduce NH_3 emissions from manure storage tanks, as both a floating cover and a manure additive to mitigate emissions [15,16]. Biochar's effectiveness is influenced by its specific properties, application methods, and dosage [17]. The production process affects biochar characteristics such as particle size, surface area, porosity, pH, and nutrient content, which can in turn significantly affect its performance [18]. Pyrolysis (particularly slow pyrolysis) tends to produce biochar with larger, more structured particles due to slower decomposition and lower operating temperatures (typically 300–700 °C). Gasification operates at higher temperatures (often 700–1200 °C) with limited oxygen, leading to finer, more fragmented particles, with higher stability and surface areas.

Acidification or bio-acidification of livestock by-products are also successfully applied to reduce NH_3 emissions [19]. Wood vinegar is a promising bio-acidifying agent that has been investigated in recent studies for its potential to reduce GHG and NH_3 emissions and to preserve N, either on its own or in combination with biochar [20]. However, investigations on the overall environmental feedback of bio-acidification are still needed, since several interactive and contrasting effects are expected to occur [19]. Furthermore, comprehensive assessments of the net environmental impact, considering the combined effects on CH_4, N_2O, CO_2, and NH_3 emissions, remain limited, with studies reporting variable effects across different greenhouse gases [21].

The primary objective of this study was to evaluate the efficacy of different treatments in mitigating NH_3 and GHG emissions during the storage of livestock by-products. We report results from three independent experiments comparing: (i) digestate versus slurry; (ii) raw digestate versus liquid fraction; (iii) biochar as a cover; (iv) biochar derived from pyrolysis versus gasification; (v) biochar application as a cover versus a mixture; and (vi) activation using wood vinegar.

The three experiments differed in lengths and treatments; therefore, not all combinations have been assessed. However, we believe the study provides a good overview of the main processes and mitigation options, considering a certain variability of tested materials.

2. Materials and Methods

2.1. Incubation Experiments

Livestock by-products were incubated in 30 L capacity tanks with hermetic seals, arranged in a completely randomized design using a random number generator. The experiment was conducted in climate-controlled greenhouses at Fondazione Minoprio. Each tank was filled with 10 L of livestock by-products, maintaining a diameter-to-height ratio representative of typical on-farm storage conditions in the Po Valley. The tanks were sealed with lids equipped with two valves for gas sampling, which were connected via tubing to a portable gas analyzer. The main characteristics of the livestock by-products and the applied mitigation treatments are summarized in Table 1.

Table 1. Composition of livestock by-products and treatments. The following abbreviations are used: C org—Organic C; TN—Total nitrogen; N-NH_4—Ammonium; H:Corg—Hydrogen–carbon ratio; Ac. Acid—Acetic acid. Bulk density of biochar was measured on raw, moist material.

Livestock By-Products	**pH**	**C org (%)**	**TN (%)**	**N-NH_4 (%)**		
Raw digestate inc. 1 (RD1)	8.1	53.1	8.79	2.73		
Raw digestate inc. 2 (RD2)	8.3	76.1	12.6	6.5		
Digestate 1 liquid fraction (DLF)	8.4	n.d.	13.9	3.31		
Slurry inc. 2 (SL2)	8.2	66.6	13.7	4.9		
Slurry inc. 3 (SL3)	7.1	40.2	9.8	3.97		
Treatments	**pH**	**C org (%)**	**TN (%)**	**N-NH_4 (%)**	**Bulk Density (kg L^{-1})**	**H:Corg**
Biochar—pyrolysis (Bp)	10.2	51.5	0.985	0.02	0.361	0.37
Biochar—gasification (Bg)	12.0	69.1	1.02	<0.001	0.204	0.19
	pH	**Ac. acid (%)**	**Total phenols (g kg^{-1})**	**Total polyphenols (g kg^{-1})**	**Bulk Density (kg L^{-1})**	**Heavy metals (mg kg^{-1})**
Wood vinegar (WV)	3.15	2.45	2.9	16	1.05	<1

Biochar produced by pyrolysis exhibited significantly larger particle sizes, with 77% exceeding 5 mm, whereas biochar from gasification was notably finer and powderier in texture. Furthermore, biochar from pyrolysis had a higher ash content (37%) than biochar from gasification (21%). Amounts of polycyclic aromatic hydrocarbons were below the maximum permissible levels for both biochar types (from pyrolysis and gasification). When activated with wood vinegar, biochar pH decreased to 7.9 and bulk density increased to 0.635 kg L^{-1}.

The following incubations were set up in tri-replicates:

Incubation 1: Effect of biochar cover on digestate (raw and liquid fraction)

The incubation was conducted in July 2023 with 8 measurements in 14 days (0, 1, 2, 3, 4, 7, 10, 14). Eighteen tanks were filled with 10 L of livestock by-product covered with

biochar from pyrolysis in layers of different heights. The tested treatments are reported in Table 2.

Table 2. Livestock by-products and treatments tested in incubation 1.

Incubation 1 Treatments	Labels
Raw digestate	RD1
Raw digestate covered with 5 cm biochar from pyrolysis	RD1_5Bp
Digestate liquid fraction	DLF
Digestate liquid fraction covered with 1 cm biochar from pyrolysis	DLF_1Bp
Digestate liquid fraction covered with 2 cm biochar from pyrolysis	DLF_2Bp
Digestate liquid fraction covered with 5 cm biochar from pyrolysis	DLF_5Bp

Incubation 2: Effect of biochar cover and bio-acidification on raw digestate and slurry

The incubation was conducted in October 2023 with 15 measurements in 59 days (0, 1, 2, 4, 7, 10, 14, 17, 21, 24, 30, 38, 45, 52, 59). Eighteen tanks were filled with 10 L of livestock by-product covered with biochar from pyrolysis in a 5 cm layer. Biochar was activated with 1 L wood vinegar (BioDea, Italy, diluted with water 1:5) 2 h before the incubation start. The tested treatments are reported in Table 3.

Table 3. Livestock by-products and treatments tested in incubation 2.

Incubation 2 Treatments	Labels
Raw digestate	RD2
Raw digestate covered with 5 cm biochar from pyrolysis	RD2_5Bp
Raw digestate covered with 5 cm biochar from pyrolysis activated with wood vinegar	RD2_5Bp_WV
Slurry	SL2
Slurry covered with 5 cm biochar from pyrolysis	SL2_5Bp
Slurry covered with 5 cm biochar from pyrolysis activated with wood vinegar	SL2_5Bp_WV

Incubation 3: Effect of pyrolysis or gasification biochar applied as cover or mixture and bio-acidification

The incubation was conducted in October 2024 with 22 measurements in 85 days (0, 1, 2, 5, 6, 7, 8, 11, 14, 19, 21, 26, 29, 32, 36, 43, 49, 57, 64, 71, 78, 85). Twenty-one tanks were filled with 10 L of livestock by-product treated with biochar from pyrolysis or gasification as cover or mixture. The gasification biochar cover and pyrolysis biochar mixture were activated with 1 L wood vinegar (BioDea, Italy, diluted with water 1:5) 2 h before the incubation start. The quantity of biochar added as cover or mixed was the same, respecting the ratio kg biochar/volume by-product = 3%, or volume biochar/volume by-product = 20%. The tested treatments are reported in Table 4.

Table 4. Livestock by-products and treatments tested in incubation 3.

Incubation 3 Treatments	Labels
Slurry	SL3
Slurry covered with 5 cm biochar from pyrolysis	SL3_5Bp
Slurry covered with 5 cm biochar from gasification	SL3_5Bg
Slurry mixed with biochar from pyrolysis	SL3_MBp
Slurry mixed with biochar from gasification	SL3_MBg
Slurry covered with 5 cm biochar from gasification activated with wood vinegar	SL2_5Bg_WV
Slurry mixed with biochar from pyrolysis activated with wood vinegar	SL2_MBp_WV

2.2. Gas Production Measurements

Gas measurements were conducted with a DX4040 FTIR Gas Analyzer (Gasmet Technologies Oy, Vantaa, Finland), which is based on infrared spectroscopy and Fourier transformation, resulting in an IR spectrum of the sample gas. The instrument is equipped with Teflon tubes with quick-connect fittings and an on-board sample pump, which has a neoprene diaphragm membrane; the maximum pressure is 1 bar and the maximum flow is 2 L min^{-1}. The instrument simultaneously analyzes 25 gases, and was previously calibrated by the manufacturer. In our study, only H_2O, CO_2, CH_4, N_2O and NH_3 fluxes were monitored. Prior to each use, the hardware status is checked, and a zero calibration is performed with pure N (99.999%). The instrument was connected to the lids with two Teflon tubes, creating a closed loop between the instrument and the tank, which allowed reliable NH_3 measurements to be obtained [22]. To measure the flux for each gas, consecutive measurements of the individual gas concentrations over time were performed for 6 min, reading gas concentrations every 30 sec, for a total of 18 readings every measurement time, to measure the increase of gas concentrations within the tank. The tanks were left open between each measurement time to avoid saturation and were closed during measurements.

To convert gas concentration (ppm) into gas flux the following equation was used:

$$\text{Gas flux } (\mu\text{mol m}^{-2}\text{ s}^{-1}) = [(dC/dt)] \times [V/(Va \times (T2/T1)] \times 1/Vs$$

where:

dC/dt is the rate of change of concentration of each gas [ppm] with time (min)

V is the volume of the vessel including cell, sample lines + headspace tank volume (free headspace was calculated for each tank)

V*a* is the molar volume for ideal gas at 273 K = 22.4 m^3 mol^{-1}

T1 is the air temperature (K)

T2 is the standard temperature (K)

Vs is the volume of substrate = 0.01 m^3

Gas fluxes were then converted to g h^{-1} m^{-3} using molecular weight of each gas. Linear interpolation was used to calculate cumulative fluxes.

Temperature within the tanks was measured at every single measurement time with a portable instrument (Hanna thermometer, Part Code HI7661), to correct gas fluxes according to the Idela Gas Law.

pH of the substrates within the tanks was measured at every single measurement time with a pH meter (InLab 413, MP220, Mettler Toledo, Columbus, OH, USA).

2.3. Statistical Analysis

Significant differences in gas production between treatments were evaluated separately for each incubation using repeated measures ANOVA across all measurement times, followed by Fisher's LSD post-hoc test ($p < 0.05$), performed with Statistica 7 software (StatSoft, Hamburg, Germany). The pH of substrates in incubations 2 and 3 was analyzed using two-way ANOVA, followed by Fisher LSD post-hoc test ($p < 0.05$).

Discriminant function analysis (DFA) was performed using NH_3, CH_4 and CO_2 emissions as grouping variables. Squared Mahalanobis distances between group centroids were determined. Two significant discriminatory roots were derived and the results of DFA were graphically presented in two dimensions.

3. Results

3.1. Incubation 1

The liquid fraction of digestate (DLF) exhibited significantly higher NH_3 emissions and lower CH_4 and CO_2 emissions (not statistically significant) compared to raw digestate (RD) throughout the incubation period (Figure 1 and Table 5). The application of a 5 cm biochar cover significantly reduced NH_3 and CO_2 emissions in both RD and DLF. These differences remained consistent over the entire incubation period for both gases. A non-significant increase in CH_4 emissions was observed in the RD treatment with the 5 cm biochar layer after the first week. N_2O emissions remained near zero, with high variability among replicates, and no significant differences were observed regardless of time, substrate, or treatment.

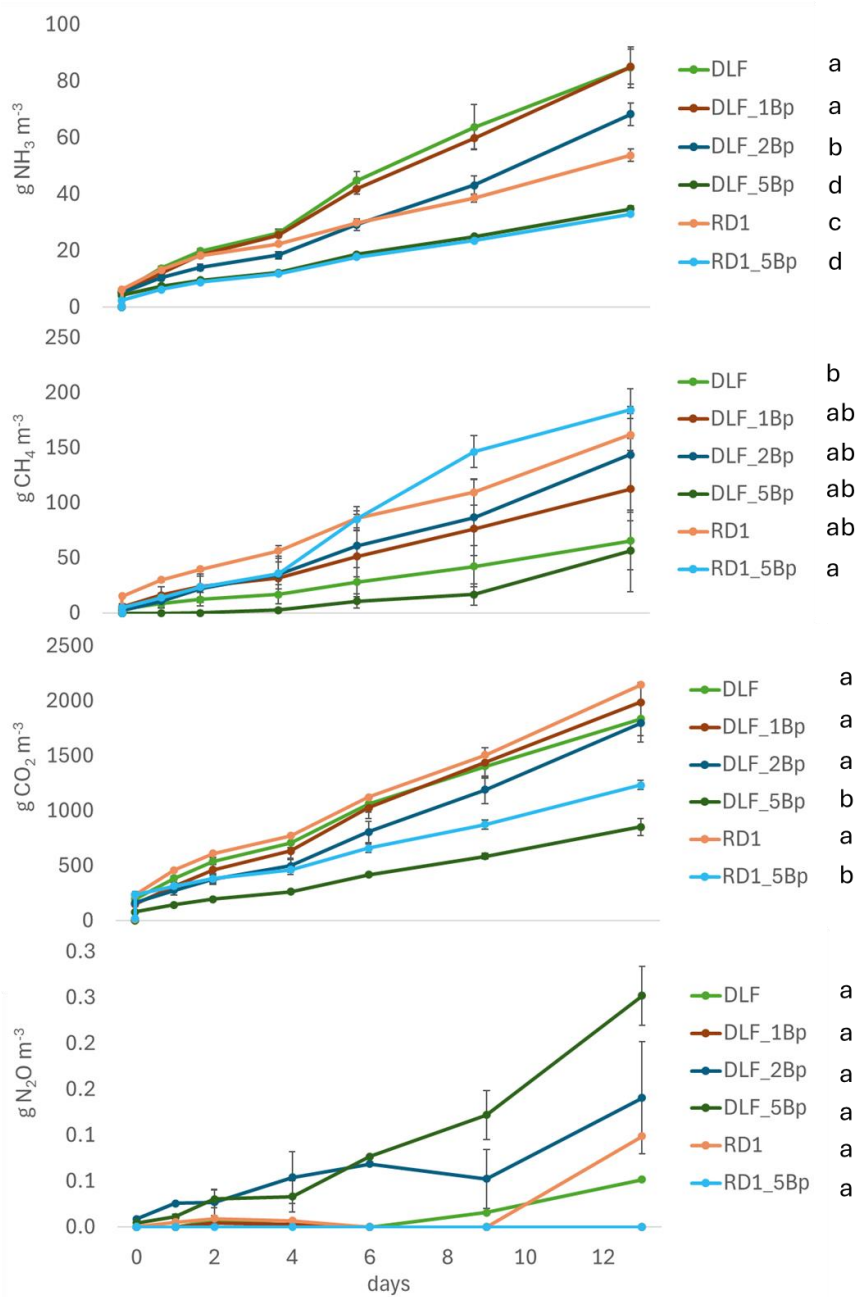


Figure 1. Cumulative emissions of NH_3, CH_4, CO_2 and N_2O (from top to bottom) measured in incubation 1. Standard errors are reported for each measurement day. Different letters indicate significant differences between treatments at $p < 0.05$ (repeated ANOVA). According to Table 2, RD: Raw digestate; DLF: Digestate liquid fraction; 1Bp, 2Bp, 3Bp: cover layer (cm) of biochar from pyrolysis.

Table 5. Percentage effects of mitigation strategies on cumulative gas production and pH at the beginning and at the end of incubations. Significant effects are reported with * (*t* test, $p < 0.05$). n.s. not significant, n.d. not determined.

	NH_3	CH_4	CO_2	N_2O	pH Initial	pH Final
DLF vs. RD	58 *	−60 n.s.	−14 n.s.	−47 n.s.	4 *	n.d.
RD vs. SL	56 *	17 n.s.	24 *	41 n.s.	3 *	−2 n.s.
Cover 5Bp (DLF)	−59 *	−13 n.s.	−53 *	384 n.s.	n.d.	n.d.
Cover 5Bp (RD)	−39 *	14 n.s.	−42 *	n.d.	n.d.	n.d.
Cover 5Bp (SL)	−44 *	42 n.s.	−50 *	−59 n.s.	2 *	−6 *
Cover 5Bp vs. MBp (SL)	−81 *	−2 n.s.	4 n.s.	485 *	n.d.	n.d.
Cover 5Bg vs. MBg (SL)	13 n.s.	329 *	214 *	326 n.s.	n.d.	n.d.
MBp (SL)	−21 n.s.	59 n.s.	3 n.s.	706 n.s.	2 *	4 n.s.
MBg (SL)	−23 n.s.	−36 n.s.	−30 n.s.	188 n.s.	14 *	1 n.s.
5Bp vs. 5Bg (SL cover)	−83 *	−43 *	−51 *	285 *	n.d.	n.d.
MBp vs. MBg (SL mixture)	3 n.s.	149 *	47 n.s.	180 n.s.	−11 *	2 n.s.
Wood vinegar (RD cover Bp)	−63 *	86 n.s.	28 n.s.	n.d.	−4 *	−5 n.s.
Wood vinegar (SL cover Bp)	−66 *	231 *	90 *	n.d.	−3 *	−6 n.s.
Wood vinegar (SL cover Bg)	−55 *	−50 *	18 *	257 *	n.d.	n.d.
Wood vinegar (SL mixed Bp)	7 n.s.	−55*	−7 n.s.	−94 n.s.	0 n.s.	−1 n.s.

3.2. Incubation 2

RD exhibited higher NH_3 and CO_2 emissions compared to slurry (SL), with a consistent trend throughout the incubation period (Figure 2 and Table 5). Methane (CH_4) emissions were similar between the two by-products. The application of a biochar cover significantly reduced NH_3 and CO_2 emissions from both RD and SL as early as the first 24 h of incubation (Table 5), but had no significant effect on CH_4 or N_2O emissions. However, a non-significant increasing trend in CH_4 emissions was observed after the first month. Wood vinegar (WV) significantly reduced NH_3 emissions from both RD and SL from the beginning of the incubation period. A sharp increase in CH_4 emissions from RD and SL was observed starting from the first week ($p < 0.05$). N_2O emissions became detectable after one month in untreated RD and SL, although no significant differences were observed at any measurement time in response to either biochar or WV treatments.

3.3. Incubation 3

Overall, incubation 3 showed higher values for all gases compared to the other incubations, even considering a comparable length. The NH_3 emissions rate showed a sharp increase within the first month of storage, reaching a maximum of 14 g m^{-3} day^{-1}. Afterward, the rate slowed down to approximately 7 g m^{-3} day^{-1}. Pyrolysis biochar effectively reduced NH_3 emissions from slurry (SL) when applied as a cover, but had no significant effect when mixed into the slurry throughout the incubation period (Figure 3 and Table 5). Methane and CO_2 emissions were not significantly affected by pyrolysis biochar, either as cover or when mixed, at any measurement time. After the first month of incubation, N_2O emissions showed a significant increase with pyrolysis biochar cover ($p < 0.05$). When added as a cover, biochar from gasification resulted in higher NH_3, CH_4 and CO_2 emissions, compared to the pyrolysis biochar, with an opposite trend observed for N_2O emissions. When mixed, biochar from gasification showed lower CH_4 emissions than biochar from pyrolysis, with this trend consistent throughout the incubation period. Gasification biochar cover significantly increased CH_4 and CO_2 emissions after the first week of incubation. Wood vinegar had variable effects depending on its application: when combined with pyrolysis biochar cover, it reduced NH_3 emissions while increasing CH_4 and CO_2 emissions; when combined with gasification biochar cover, it reduced NH_3 and

CH_4 emissions but increased CO_2 and N_2O emissions; and when mixed with biochar, it only reduced CH_4 emissions.

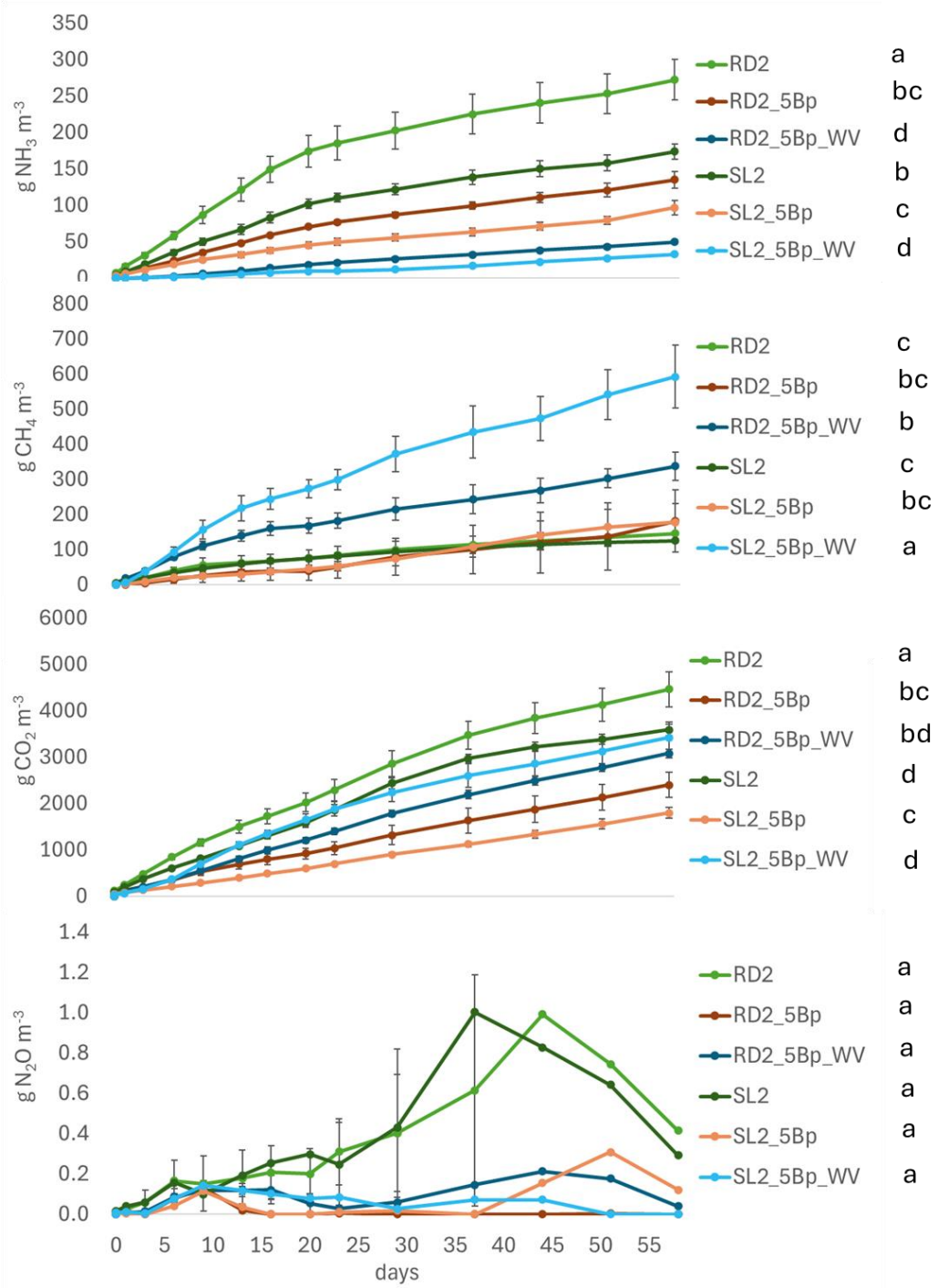


Figure 2. Cumulative emissions of NH_3, CH_4, CO_2 and N_2O (from top to bottom) measured in incubation 2. Standard errors are reported for each measurement day. Different letters indicate significant differences between treatments at $p < 0.05$ (repeated ANOVA). According to Table 3, RD: Raw digestate; SL: Slurry; 5Bp: 5 cm biochar from pyrolysis; WV: Wood vinegar.

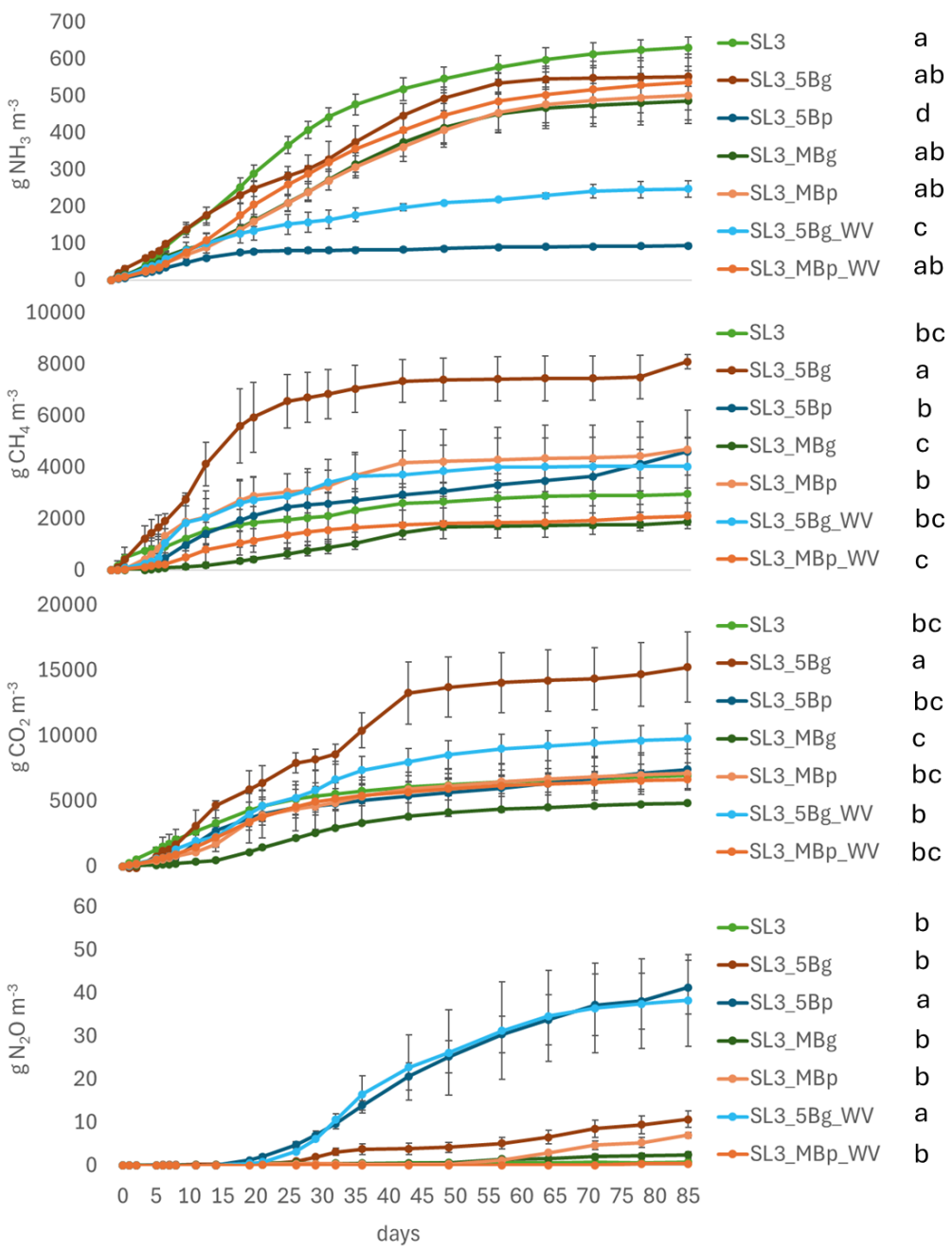


Figure 3. Cumulative emissions of NH_3, CH_4, CO_2 and N_2O (from top to bottom) measured in incubation 3. Standard errors are reported for each measurement day. Different letters indicate significant differences between treatments at $p < 0.05$ (repeated ANOVA). According to Table 4, SL: Slurry; Bp: 5 cm biochar from pyrolysis: Bg: biochar from gasification; 5B: 5 cm biochar cover; MB: Biochar mixed; WV: Wood vinegar.

3.4. pH Variations

The pH of the tested by-products followed the order: DLF > RD > SL SL used in incubation 3 had significantly lower pH compared to SL used in incubation 2 (Tables 1 and 4). At the start of the incubations, biochar cover increased the pH of RD and SL, while mixed biochar only increased pH when derived from gasification (Figure 4). pH was significantly lower at the beginning of incubation in RD and SL treated with wood vinegar, but no significant difference was observed at the end of the incubation (Figure 4).

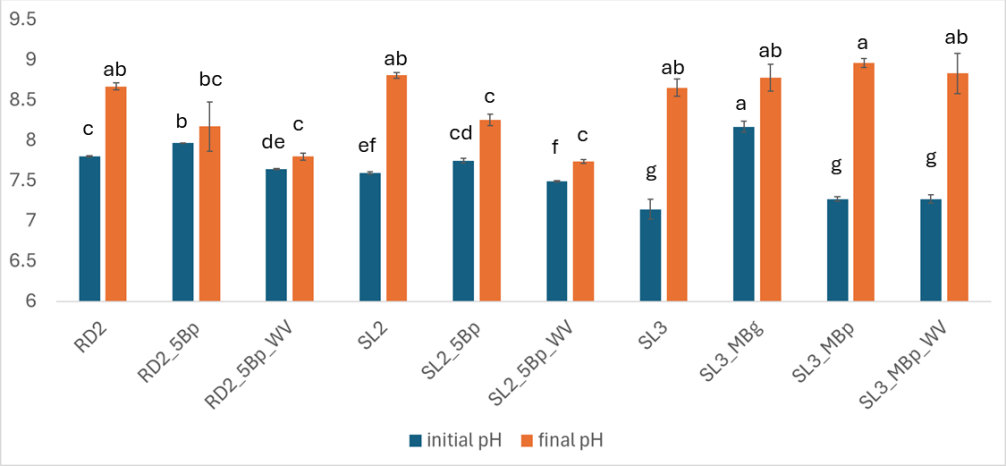


Figure 4. pH values at the beginning and at the end of incubations 2 and 3. Standard errors are reported. Different letters indicate significant differences between treatments at $p < 0.05$.

3.5. Discriminant Function Analysis

Discriminant function analysis showed a clear separation between slurries used in incubation 2 and 3 and between digestates used in incubation 1 and 2 (Figure 5). Raw and liquid fractions of digestate used in incubation 1 were not different, and nor were those treated with 1 and 2 cm biochar cover. All by-products treated with a cover of 5 cm biochar from pyrolysis were well separated, forming a group with DLF, RD1, RD2 and SL2, and another group with SL3. The addition of wood vinegar further separated SL2 and RD2. By-products treated with mixed biochar from pyrolysis and with biochar from gasification formed distinct groups, with and without the addition of wood vinegar.

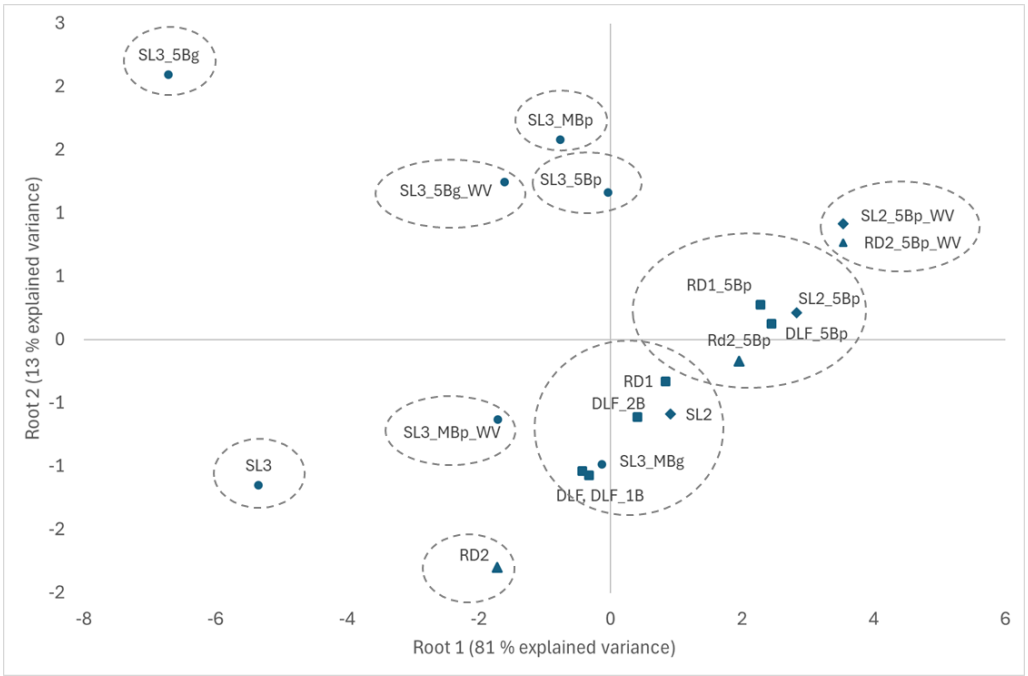


Figure 5. Discriminant function analysis using NH_3, CH_4 and CO_2 cumulative emissions of the three incubations at 14 days as independent variables. Explained variance of Root 1 and 2 is reported in the figure. Squared Mahalanobis distances are represented by dotted circles, indicating significant differences among treatments when not overlapping ($p < 0.05$).

4. Discussion

Overall, the three incubations revealed distinct patterns of gaseous emissions from livestock by-products, highlighting varied responses for each gas depending on the type of compound, storage duration, and applied treatment.

The duration of storage played a pivotal role in determining the environmental impact of livestock by-product storage. High rates of NH_3, CH_4, and CO_2 emissions were observed during the first month of storage, aligning with previous findings by [23] for NH_3 and by [24] for both NH_3 and CH_4. Prolonged storage also led to N_2O emissions, which only became significantly different from zero after the first month in incubations 2 and 3. In line with this, several studies have reported negligible N_2O emissions during short-term storage [25,26]. This suggests that reducing storage duration could be a highly effective strategy for mitigating emissions.

Processing slurry through anaerobic digestion represents a win–win strategy, offering several significant benefits: (i) it eliminates the need for prolonged storage between slurry production and soil application, (ii) it enables the utilization of a portion of organic matter as biofuel, and (iii) it produces an N-enriched material [27,28]. In fact, digestate exhibited a higher N-NH_4 content, which was further concentrated in the liquid fraction (Table 1). However, NH_3 emissions exhibited a distinct hierarchy: slurry < raw digestate < liquid fraction correlated to NH_4 availability. Regardless of C concentration, an inverse trend emerged for both CH_4 and CO_2. This pattern underscores two critical requirements: (i) simultaneous measurements of all gases to ensure reliable estimates, and (ii) tailored strategies targeting the primary loss pathways for each by-product.

Biochar application is increasingly recognized as a promising strategy [28,29], particularly when activated with acids [30], for mitigating NH_3 emissions during the storage of livestock by-products. This study further enhances our understanding of biochar's effectiveness by examining the influence of biochar type and application method. Notably, the thickness of the biochar layer plays a crucial role: layers of 1 or 2 cm thickness did not significantly affect NH_3 and GHG emissions, regardless of the treated by-product. However, a 5 cm thick surface layer proved effective in reducing NH_3 emissions by up to 60% from the liquid fraction of digestate. The significant effect of the biochar cover was not influenced by the increase in pH, which was transient and observed only at the beginning of the incubation period. Similar results were reported by [31], who created a semi-porous crust layer over the surface of manure, affecting mass transfer to the headspace. Biochar's porosity and sorption capacity, including its ability to absorb ammonium, are well-documented [32].

These characteristics help explain the differences in the effectiveness of pyrolysis and gasification biochar. Visual observations revealed that biochar produced via pyrolysis demonstrated superior performance, as its floating cap structure remained stable during storage, whereas the biochar derived from gasification tended to partially submerge over time. Accordingly, the cover with pyrolysis biochar proved more effective than the cover with gasification biochar in reducing NH_3, CH_4 and CO_2 emissions. This difference can be attributed to the distinct physicochemical properties imparted by the two processes: pyrolysis biochar typically exhibits greater structural integrity and larger particle size, while gasification biochar is generally more powdery and less cohesive, leading to reduced buoyancy and stability during storage, in addition to potential problems related to being blown or moved by the wind if placed outdoors [18,33].

In contrast, when incorporated as a mixture, neither pyrolysis nor gasification biochar significantly mitigated gaseous emissions. When biochar is added as a cover, it may act as a physical barrier to gas diffusion, potentially limiting microbial activity beneath the cover. Conversely, mixing biochar into the substrate increases soil porosity and aeration,

facilitating O_2 diffusion throughout the substrate and supporting aerobic microbial processes. The observed increase in CH_4 emissions when using gasification biochar as a surface cover, compared to its incorporation into the substrate, could be primarily attributed to the preservation of anaerobic conditions beneath the cover. These conditions, combined with the presence of nutrients and carbon, likely stimulated methanogenic communities under anaerobic conditions [34].

Pyrolysis biochar covers also increased N_2O emissions from slurry at the end of incubation 3, compared to both incorporated pyrolysis biochar and gasification biochar. Limited data are available on N_2O fluxes from stored livestock by-products, as long incubation periods are required to observe non-negligible fluxes [23]. N_2O peaks are typically influenced by pH, oxygen, and substrate availability in localized hotspots that may have occurred in the biochar cover layer. However, based on our data, it is not possible to draw broad generalizations.

Wood vinegar-activated biochar cover was effective in reducing NH_3 emissions by up to 66%, both for slurry and digestate, as reported by [20,35]. Wood vinegar is a pyrolysis by-product that is mainly constituted by acetic acid and phenols [36]. Wood vinegar demonstrated an acidification capacity (Tables 1 and 5) that effectively reduced NH_3 emissions while retaining N-NH_4 content, highlighting its potential as a promising approach for producing N-rich organic fertilizers.

The surface application of wood vinegar-activated pyrolysis biochar significantly increased CH_4 and CO_2 emissions. Wood vinegar can stimulate methanogenesis in anaerobic environments, primarily due to its high content of readily biodegradable organics, especially acetic acid, which is a direct substrate for acetoclastic methanogenesis [37]. Furthermore, studies by [38] have shown that, at moderate organic loading rates, wood vinegar additions increase the abundance and activity of methanogenic archaea, particularly those associated with acetoclastic pathways. Slurry environments, characterized by high labile C content, abundant substrates, and anaerobic conditions, likely intensified acetoclastic methanogenesis, causing a peak in CH_4 production. This CH_4 surge offset NH_3 mitigation efforts achieved through acidification. Notably, this trade-off occurred only with pyrolysis biochar covers, not with (i) incorporated biochar mixture or (ii) gasification biochar applications, which reduced CH_4 emissions. Low H:C and high C:N ratios are reflective of biochar recalcitrance [39]. The differing effects of pyrolysis and gasification biochar when activated with wood vinegar likely arise from a complex interplay between biochar recalcitrance, substrate availability, and pH conditions. This interaction also influenced the observed increase in N_2O emissions associated with wood vinegar-activated gasification biochar covers. Therefore, further research is necessary to fully elucidate the underlying mechanisms, as our current data did not provide a comprehensive explanation.

In conclusion, the results of this study suggest that using pyrolysis biochar as a cover layer, with a thickness of 5 cm (equivalent to 3% w/v), is more effective than incorporation. The pyrolysis biochar is preferable, as: (i) it provides the highest benefits, (ii) it creates a more stable cover, and (iii) the pyrolysis process produces both biochar and wood vinegar. For N-rich by-products, such as the liquid fraction of digestate, it is recommended to activate the biochar layer with wood vinegar or another organic acid. However, for slurry or substrates with high methanogenesis potential, adding acetic acid is not advised due to the potential negative impact on CH_4 emissions.

Further research is warranted to explore the differences between pyrolysis and gasification biochar, as well as the potential benefits of activating biochar with wood vinegar or other organic acids. By investigating the nuances of pyrolysis versus gasification biochar and the activation process, we can unlock new pathways for improving soil health, reducing greenhouse gas emissions, and promoting a circular economy.

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Abbreviations

The following abbreviations are used in this manuscript:

NH_3	Ammonia
CH_4	Methane
CO_2	Carbon dioxide
N_2O	Nitrous oxide
GHG	Greenhouse gas
N	Nitrogen
PM	Particulate matter
NVZs	Nitrate vulnerable zones
OM	Organic matter
C	Carbon
C org	Organic C
TN	Total nitrogen
$N\text{-}NH_4$	Ammonium
H:Corg	Hydrogen carbon ratio
Ac. acid	Acetic acid
ANOVA	Analysis of variance
DFA	Discriminant function analysis

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