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# Evaluating Ammonia Reduction Efficiency of Natural Covers in Buffalo Manure Digestate Management: A Techno-Economic-Environmental Perspective on Biochar Implementation

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## Abstract

Storage of livestock effluents represents a major source of ammonia ($NH_3$) emissions to the atmosphere. Therefore, identifying efficient and sustainable mitigation strategies is crucial. Conventional floating covers are commonly used to reduce emissions; however, they often present limitations in terms of management, durability, and cost. This study proposes a novel approach by comparing traditional floating cover materials like natural crust, straw, and light expanded clay with biochar as an innovative mitigation strategy to reduce ammonia volatilization from the liquid fraction of buffalo digestate obtained from an anaerobic digestion plant in southern Italy. All cover materials were applied at a uniform thickness of 2 cm under laboratory conditions using a dynamic chamber technique. Additionally, a cost analysis was performed considering the material purchase cost for an average storage tank of 700 $m^2$ and two hypothetical reduction efficiencies (50% and 70%). Results indicated that biochar was the most effective cover, achieving a 67% reduction in ammonia emissions compared with the natural crust. Light expanded clay exhibited the lowest efficiency, likely due to its insufficient sealing capacity at the applied thickness. From an economic perspective, biochar becomes increasingly competitive when emission reduction efficiency is accounted for, owing to its favorable physical–chemical properties. Further research is recommended to evaluate the long-term durability of biochar as a cover material and to investigate potential synergistic effects when applied later as a soil amendment.

**Keywords:** ammonia emission reduction; digestate storage; techno-economic prospect; dairy buffalo

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## 1. Introduction

Approximately 81% of the total worldwide emissions of ammonia (NH3) are caused by activities in the agricultural sector [1]. Specifically, livestock farming contributes to the production of 60-90 % of the NH3 emissions produced from agriculture [2–3]. Once NH3 is volatilized, generate negative effects on the environment, in particular on soil, air and water [4]. Moreover, ammonia volatilization is also responsible for the formation of secondary particulate matter (PM 2.5) responsible for human illnesses, such as cardiovascular disease [5]. Livestock activities generate large quantities of manure, which must be stored before being used as fertilizer to comply with Nitrate Action Programs (NAPs) developed by EU Member States, which set strict guidelines for the management of organic and inorganic nutrients, restricting storage, rate and timing of land application to reduce diffuse nutrient losses from agricultural sources. Ammonia emissions from stored manure depend on the characteristics of the manure, storage conditions, management practices, temperature, and climate.

Higher temperatures increase emission intensity and variability, with peak emissions typically occurring during the central hours of the day [6–8]. The National Emission Ceilings Directive (NEC Directive) in the European Union demands studies and applications of efficient technologies to reduce $NH_3$ emissions from agricultural methods, and verifies the efficacy of these technologies [9]. Researchers have focused significant attention on the issue of ammonia emissions in the livestock sector, seeking mitigation strategies. Public agencies, regulators, and farmers are recognizing the environmental impact of ammonia emissions and the need to reduce them. One potential solution is applying covers to slurry during storage to reduce $NH_3$ emissions [10–12]. The exposed surface of manure can be covered with different materials, natural or synthetic. Covers application can reduce ammonia emissions by decreasing air or wind action, and keeping the nitrogen in the manure by decreasing the mass transfer from the manure to the free air [13–15]. Permeable and organic covers are susceptible to weather conditions and can sink or drift, blocking pumping drainage systems [16,17]. Natural covers, unlike synthetic ones, don't require removal of meteoric water. They are typically low-cost and effective in emission reduction, with organic covers achieving up to 87% reduction [18]. Several natural materials are suitable for this purpose. Straw, for instance, is a crop residue, that if already present on-farm as leftover, can be considered a low-cost material. Research studies have demonstrated that the application of straw, whether untreated or pretreated, as a material on stored manure, has the capacity to significantly reduce ammonia emissions [15,19]. Also, when reed straw was added to manure during the composting process, a reduction of circa 12 % was registered. This outcome is probably consequent to the fact that straw is a N-poor material and can immobilize ammonia [14]. However, it should be noted that straw is a material with a low density, it is susceptible to damage from wind and rain, and can sink. Consequently, numerous studies have evaluated the straw's capacity to maintain its position in relation to its effectiveness in reducing ammonia emissions [18]. In order to prevent straw from sinking into the stored slurry, the total solids of the slurry should be at least 4% [18]. Although different straw types have been assessed in literature such as reed straw, wheat straw, and rice straw, a comparison between the different aptitude and efficacy in reducing the emission between these different materials has not been assessed yet.Studies have shown that adding straw (either untreated or pretreated) to stored manure can significantly reduce ammonia emissions. However, due to its low density, straw is susceptible to wind and rain damage, and can sink into the slurry. To prevent this, the slurry should contain at least 4% total solids. Various types of straw have been studied, including reed, wheat, and rice, but no comparison has been made of their effectiveness in reducing ammonia emissions [18,19]. Clay is a low-cost, porous, water-impermeable mineral that is commonly used as an insulating material. It can float on liquid surfaces, such as slurry [16]. Light expanded clay aggregates (LECA®) are an inexpensive option for covering slurry [17]. However, their effectiveness in reducing ammonia emissions is inconsistent. LECA® granules only reduce ammonia emissions when applied at a thickness of 14 cm. Thinner layers may be less effective and can increase $NH_3$ volatilization [12]. Additionally, the surface of LECA® promotes microbial growth, which can degrade organic matter and increase $NH_4^+$ release and $NH_3$ emissions. This microbial activity can lead to bio-plugging of the LECA®, further reducing its performance [16,20].

Biochar, a material produced by the pyrolysis of various biomasses, has gained attention as a method of reducing ammonia emissions when applied to stored livestock manure. In addition to its use in agriculture, biochar is employed in nutrient recovery, livestock farming, pharmaceuticals, and water treatment [21,22]. Biochar is obtained from the pyrolysis of different biomasses [23]. The pyrolyzed biomass material as well as the pyrolysis conditions and processes can influence the final characteristics of the biochar. Generally, the peak temperature and heating rate are the factors analysed the most [24]. The benefit that biochar brings to the soil when applied as a soil conditioner has made biochar widely studied in the last years [25]. In addition, its effectiveness in reducing the emission of $NH_3$ when used as a cover on stored livestock manure is due to the fact that it acts as a physical barrier and has an adsorption effect [26]. The characteristics of biochar, including its chemical functional groups, porosity, surface area, and hydrophobicity, affect its ability to absorb

$NH_3$ and ammonium ions ($NH_4^+$). Its hydrophobic nature enables it to float on manure and reduce liquid absorption [27–29]. Studies show that biochar acts as a physical barrier and an adsorbent, effectively reducing ammonia emissions. When applied to swine manure, a biochar cover reduced ammonia emissions by 33%. Other studies have reported reductions ranging from 4% to 78%, depending on the biochar's properties and production methods. However, weather conditions and manure characteristics can influence biochar's performance [29,30]. Researchers are continuing to study its potential for large-scale applications and how different pyrolysis processes impact its effectiveness[31].

Biochar production is generally related to a local niche industry and large-scale producers are not widely common [22]. Though biochar fits well in the circular economy concept, economic viability and market competitiveness are necessary to facilitate broader-scale biochar production and agricultural sector adoption [32]. Biochar is not a single, uniform product. Its physicochemical characteristics can vary significantly. Consequently, its purchase and selling prices can differ widely based on these properties The low market demand for biochar presents a significant challenge to the generation of profit from its production. Furthermore, the market value of the subject has yet to be thoroughly established [32,33]. To date, only a few studies have examined the effectiveness of natural cover materials in reducing ammonia emissions from stored buffalo manure [28–34]. This study aims to compare the effectiveness of different cover materials in reducing ammonia emissions from buffalo slurry, a type of livestock waste that has been investigated less frequently in this context. Although previous studies have produced mixed results, this work provides a clear comparison of the effectiveness of different cover materials in mitigating ammonia emissions from buffalo manure, thereby contributing to a better understanding of this issue.

## 2. Materials and Methods

### *2.1. Experimental Setup*

The efficiency in reducing ammonia emissions of three natural floating covers from the stored liquid fraction of buffalo digestate was tested for 34 days under laboratory conditions. Each experimental unit, used to simulate the average storage situation of farm tanks, consisted of a 5 L capacity glass pot, with a height of 25 cm and diameter of 16 cm. Each pot was filled with 3 l of liquid fraction of digestate. The following materials, corn straw, biochar, and clay LECA® were tested in triplicate. Before the weighing and the application, all the covering materials were air dried at 105°C for 24 hours to remove any moisture accumulated during their storage. The different covers were brought to room temperature before the application. All cover layers were standardized at a thickness of 2 cm, ensuring a consistent basis for comparison with the biochar layer [35]. To measure the thickness of each cover (2 cm), an empty container of the same type was used to store the liquid digestate was used. The thickness was measured using a tape measure and the material was weighed before application. The straw cover was manually pressed to the bottom of the jar to create a stable, uniform layer, enabling a direct comparison with other cover materials. After the glass pots were filled with digestate (3L) the covers were manually applied to the digestate surface providing a layer of 2 cm, respectively 12.8 g of straw (S), 84 gr of biochar (B), and 180 gr of clay LECA® (L). Also, a control experimental unit (NC) consisting of only digestate without any cover was set up, for a total of 12 jars. The experimental units were stored during the whole test period in a walk-in closet with a constant temperature set at 18°C. The storage and gas measurements were carried out in a controlled environment.

### *2.2. Buffalo Digestate Characteristics and Analysis*

The plant, located in Caserta province, treats the buffalo slurry produced in the surrounding buffalo farms specialized in milk production. The liquid fraction of the digestate was collected right before it entered the storage tank and was immediately transported to the laboratory facility to be characterized for the determination of chemical and physical properties, such as pH, Dry Matter

(DM), Total Kjeldahl Nitrogen (TKN), Total Ammoniacal Nitrogen (TAN) according to Standard Methods [36]. Samples were also taken at the end of the storage period. All the analyses were carried out in duplicate. Digestate DM was determined by drying the digestate in an oven at the temperature of 105°C for 24 hours. The digestate TKN content was assessed by applying the Kjeldahl method. The TAN content was defined after distillation of the digestate sampled using a titrimetric method.

### *2.3. Cover Materials Characteristics*

The biochar was purchased from Nera Biochar Srl and used in a study carried out by Scotto di Perta et al., 2020 [26] . The pyrolyzed biomass was made from wood chips from Piedmont: Elm tree, Ash tree, Chestnut and conifers. The production process consisted of a 30-minute pyrolysis at a temperature of 550° C. Table 1 summarizes biochar characteristics [34].

**Table 1.** Biochar characteristics. BET: Surface Area: Brunauer–Emmett–Teller.

| Ash wt% db | C wt% db | H wt% db | N wt% db | O wt% db | pH | OH groups mmol/g | BET* m2/g |
|---|---|---|---|---|---|---|---|
| 3.4 | 74.6 | data | 2.0 | 19.3 | 10 | 0.0697 | 350 |

LECA® (Light Expanded Clay Aggregate) clay tested, this is a 100% inert material, with an average diameter of 10 mm – 20 mm. LECA® is reported as a material resistant to high temperatures, moisture and chemical agent attacks. Moreover, the iron oxides present in the clay mineral structure can act as a catalyst for the chemisorption of Hydrogen Sulphide ($H_2S$), Ammonia, Methane and several other organic compounds.

The corn straw utilized in this experiment was obtained from a dairy cattle farm in southern Italy, where it was primarily employed as bedding material for the weaning of calves and in select other areas of the farm. Subsequent to collection, the straw underwent manual trimming to a length of approximately 2 centimetres.

### *2.4. Ammonia Emissions Measurement*

To define the effect of different treatments on ammonia emissions during manure storage under controlled experimental conditions, the ammonia emissions were measured following the dynamic chamber method described by [15]. Specifically, the jars were only sealed during the measurement process to allow ventilation of the headspace. To seal the containers, a screw cap was used that was designed to facilitate airflow and connect the container to an expansion chamber. The flow rate was regulated using a flow meter. An air exchange rate of 1.5 L min$^{-1}$ was achieved using a vacuum pump. Prior to sampling the ammonia, the pump was activated for 20 minutes to stabilise the conditions. The digestate was stored accordingly in open vessels with no lid in a temperature-controlled room. Then, air was sampled for 16 minutes and analysed in real time using a gas-sensitive semiconductor sensor. (Aeroqual Series 500) to quantify NH3 concentration. The instrument produced by Aeroqual Limited of New Zealand has detection range from 0-100 ppm, with a detection limit of 0.2 ppm and an accuracy of ±0.5 ppm + 10%. The measurement occurred on days 1, 2, 6, 9, 13, 16, 20, 23, 27, 30, and 34, for a total of 11 measurements in 34 days. To maintain consistency and reduce variability, measurements were conducted in a fixed sequence, preserving a constant interval between successive samples. The pH and the manure temperature were monitored before the gas detection started. To avoid disturbance of the sample surface due to the pH probe immersion in the liquid, a plastic tube was applied to the jar wall, before the fulfilment with manure, to create easy access. The tube was therefore closed with a plastic cap and opened just during the pH measure. The pH was measured with a portable pH meter (MT51302523, Mettler Toledo).

### 2.5. Flux Calculations

The gaseous emission fluxes were evaluated as follows:

$$\boldsymbol{F} = \boldsymbol{Q}\,\frac{\boldsymbol{Cout} - \boldsymbol{Cin}}{\boldsymbol{A}} \qquad (1)$$

$C_{in}$ is the gas concentration of air inlet into the chamber in mg m$^{-3}$; $C_{out}$ is the gas concentration of air outlet from the chamber in mg m$^{-3}$; Q is the airflow rate through the chamber in m$^3$ h$^{-1}$; and A is the circular area of the emitting surface in m$^2$. Cumulative emissions from each manure type over the storage period were evaluated by averaging net flux rates between two sampling points and by multiplying by the time interval between sampling points [15].

The emission factor (EF) was defined as the percentage of N applied as digestate that is emitted as $NH_3$, as described by [29].

The emissions reduction efficiency (RE) was calculated using the formula expressed by [35].

$$\boldsymbol{RE}\% = \left[\frac{E_{treatment} - E_{control}}{E_{control}}\right] \times \mathbf{100} \qquad (2)$$

$E_{treatment}$ and $E_{control}$ refer to cumulative emissions of treated (covered) and control samples, respectively.

### 2.6. Statistical Analysis

The data collected during the observation periods were then organized into datasets, with cumulative $NH_3$ emissions calculated for each treatment. Statistical analysis was performed using one-way analysis of variance (ANOVA) followed by a post hoc Tukey test to identify significant differences between treatments. A p-value threshold of $< 0.05$ was employed for hypothesis rejection, indicating a significant difference in ammonia emission reduction across treatments. The cumulative emissions were analysed at 24 hours, on the 9th day, and on the 34th day of the measurement period. All statistical analyses were conducted using IBM SPSS Statistics for Windows (Version 28.0, IBM Corp., Armonk, NY).

### 2.7. Comparative Analysis

A scaling-up calculation was conducted considering a full-sized manure storage tank, followed by a purchasing prices comparison across the tested materials. The comparison of biochar, straw and clay was performed considering the same reduction efficiency (RE). Two hypotheses were considered: namely RE of 50% (RE50) and 70% (RE70) were chosen. Bibliographic research was conducted to build correlation between thickness of covers and ammonia RE. For the analysis, difference in slurry type, temperature and storage duration were not considered. In the selected data, thickness and RE were explicitly stated. In Table 2 used data are reported with corresponding reference.

**Table 2.** Data used to build the relationship between thicknesses (cm) of different cover materials and relative reduction efficiency (RE). Negative values indicate an enhancement of ammonia emissions.

| Materials | Slurry type | Layer thickness cm | RE % | References |
|---|---|---|---|---|
| **Biochar** | Cattle slurry | 5 | 72-82 | [30] |
| | Pig slurry | 0.635 | 16-25 | [37] |
| | Buffalo digestate | 2 | 67 | This work |
| **LECA®** | Cattle slurry | 7 | 17 | [18] |
| | Pig slurry | 14 | 75.1 | [18] |
| | Buffalo digestate | 2 | -13 | This work |
| | Pig slurry | 7 | 77 | [38] |
| **Straw** | Pig slurry | 7 | 34 | [18] |
| | Pig slurry | 14 | 86 | [18] |
| | Buffalo slurry | 1 | 7 | [39] |
| | Buffalo digestate | 2 | 36 | This work |

Data were interpolated to retrieve the covers thickness necessary to reach a specific RE for all the materials. For the purpose, both logarithmic and exponential trend lines have been used when appropriate, depending on the R2 value. These calculations were undertaken not only to determine the optimal thickness and associated costs of covers for the storage tanks but also to define the storage volume of the materials and transportation considerations. The calculation was carried out considering a manure storage tank with an emitting surface of 700 m2 corresponding to the average dimensions for a storage facility inside a buffalo farm with about 300 lactating animals, that is the average size of a buffalo farm in the region where samples were taken.

## 3. Results and Discussion

### *3.1. Manure Composition*

Digestate characteristics before and after the trial are reported in Table 3

**Table 3.** Digestate characteristics before and after the trial. Cattle slurry properties at the beginning (Before Exp) and at the end of the experiment (After Exp). NC, control; B, biochar; S, straw; L, LECA®.

| | | DM | TKN | TAN | pH |
|---|---|---|---|---|---|
| | | g/kg | | | |
| **Before Exp** | **Digestate** | 66.66 | 3.5 | 1.66 | 8.2 |
| **After Exp** | **NC** | 81.3 | 2.9 | 1.1 | 8.4 |
| | **B** | 76.2 | 2.9 | 1.3 | 8.1 |
| | **S** | 75.0 | 2.9 | 1.2 | 8.3 |
| | **L** | 73.4 | 3.1 | 1.4 | 7.7 |

As reported in Table 3, at the end of the experiment, DM values increased in all the tested samples. As a matter of fact, during the storage period, water evaporation occurred and a consequent decrease in weight and digestate level was registered in all the samples, affecting the final DM content. In line with this, the cover applications proved to influence the evaporation of the stored digestate. The highest DM increase of 22% was registered in NC, and the lowest 10% in L. As shown in Figure 1 at the beginning of the experiment the pH of the untreated manure was 8.3. The lowest value of pH was detected on the 16th day of storage; the decrease occurred in all the samples, but clay showed the lowest value.

The same day was also registered a decrease in digestate temperature. On the 30th day, the highest peak of pH occurred in all the monitored samples, shifting from a mean of 8.5 to a mean of 8.92. Generally, manure covered with clay had the lowest pH values.

With regard to the nitrogen content (TKN), a decline was observed in all the samples at the conclusion of the experiment. A less marked decrease was observed in L, with a decline of 11.4% being recorded. The reduction register for all other treatment, inclusive of NC, accounted for 17.1%. As with TKN, TAN content exhibited a similar trend across the various treatments. The reduction in TAN content was found to be lowest in L and highest in NC, at 15.7% and 33.7%, respectivelyThis section may be divided by subheadings. It should provide a concise and precise description of the experimental results, their interpretation, as well as the experimental conclusions that can be drawn.

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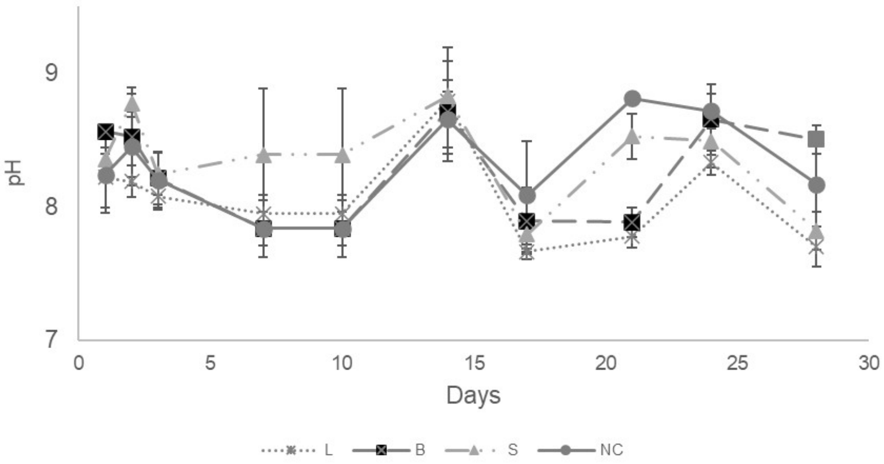

**Figure 1.** pH trends of digestate covered with clay (L), straw (S), biochar (B), and natural crust (NC), during the monitored period.

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### *3.2. Ammonia Emissions*

The cumulative $NH_3$ emission at the end of the trial (34 days) accounted 4.1, 8.1, 14.3, 12.6 gN-$NH_3$ $m^{-2}$ for B, S, L and NC, respectively. Table 4 shows the cumulated ammonia emission during the trial; all the treatments had the same emission pattern showing their effectiveness in mitigating ammonia emissions from the first hours of measurement.

**Table 4.** Mean cumulative NH3 emissions ± Standard Deviation during the experimental period, calculated at 24 hours, 9 days, and 34 days.

| **Time steps** | **24 hours** | **9 days** | **34 days** |
|---|---|---|---|
| | g $NH_3$-N $m^{-2}$ | | |
| Treatment | | | |
| **NC** | $0.7^a \pm 0.1$ | $4.0^a \pm 0.3$ | $12.6^a \pm 0.4$ |
| **B** | $0.0^b \pm 0.0$ | $0.3^b \pm 0.1$ | $4.1^b \pm 0.3$ |
| **S** | $0.4^c \pm 0.0$ | $2.1^c \pm 0.3$ | $8.1^b \pm 1.3$ |
| **L** | $0.5^c \pm 0.1$ | $3.6^a \pm 0.2$ | $14.3^a \pm 1.2$ |

B was the most effective cover material emitting 67% less than NC after 34 days ($p<0.05$), resulting also in the highest RE shown in Table 3. During the trial, the biochar cover remained visibly intact in all replicates, with no cracks or breaks forming on the surface. Although the biochar slowly sank and settled unevenly over time, particularly noticeable two weeks after application, its surface layer remained unbroken and continuous throughout the observation period. The data obtained are broadly consistent with the major trends showing that biochar cover can be effective in mitigating $NH_3$ emissions [27]. In good accordance with our findings [40] assessed a significant reduction ($p<0.05$) in $NH_3$ emission during the trial with an application of 1.5 cm of biochar cover on swine

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manure. The same mitigation effect was not registered when a thinner layer of 1 cm and 0.75 cm of this material was tested [13,22,41]. Other authors assessed that superficial biochar application reduced the cumulative ammonia emissions by 48% compared with the control [42]. In other studies, the possibility of making a second application was investigated due to the temporary effect of the biochar [37]. A reapplication of biochar, therefore a thicker cover resulted in a much higher percentage statistically significant reduction [41]. This finding suggests that biochar cover could be a good method to reduce ammonia emission when it is able to create over the manure surface a layer thicker enough to influence mass transfer to the headspace.

In the present work straw cover showed a good mitigation effect as well as a good floating aptitude. Indeed, S that was compacted by pressing before the application on the manure surface, started to decrease in density after the first week, showing on the second week a different distribution on the surface. Just the layer in contact with the manure surface appeared to be wet, but the cover did not sink before day 23. This result is however in contrast to a previous study [39] where the application of straw on stored manure did not significantly reduce $NH_3$ emissions after 6 days. Indeed, straw cover started to sink after the beginning of the trial. This difference in the cover behaviour could be addressed to different manure characteristics, particularly DM content, or more probably to the thermal pretreatment that was applied to the cover before the test.

Overall, S showed an emission reduction of 36% ($p<0.05$) compared to NC during the first 24 hours. In accordance with our findings [18] show a significant ($p<0.5$) emission reduction of 86% registered when 14 cm of this material was applied; the application of 7 cm showed a reduction of 32% ($p>0.05$). On the contrary, other tests assessing a layer of 8 cm of treated and untreated straw showed a good emission reduction compared to the control ($p<0.05$) [13]. Furthermore, straw was shown to be effective in mitigating ammonia emission in combination with zeolites not only during manure storage but also during the composting process [43]. When a layer of 30 cm of straw was applied on the manure surface during a pilot scale experiment, after 122 days of storage, the cumulative emissions were reduced by 90% compared to the control [44] showing how a thicker cover layer can enhance its capacity to mitigate ammonia emissions. All the cited authors demonstrated the feasibility of using straw cover to reduce ammonia emissions. Different layer thicknesses and pretreatment are all factors influencing the reduction efficiency.

Regarding the jar covered with LECA®, after 24 h of storage L reduced the emission by 29% compared to the control ($p<0.05$), proving to have the lowest reduction efficiency between the treatments.

From day 2 to day 13 the cover's effectiveness continued to decrease (Figure 2). At the end of the trial, L showed the lowest RE (Table 4). For the whole trial duration, L was the only cover to remain physically stable. This phenomenon may have occurred because its capacity to float was not affected by the contact with the manure; LECA® pebbles always showed a part of its surface under the manure level and another part above the manure surface. The applied granules managed to totally cover the manure surface with a single layer of LECA® sphere. Throughout the trial, the granules were incorporated into the manure surface creating a solid cover, less mobile than the other tested. The higher cumulative ammonia emissions related to L was consistent with a previous study also reporting an increase in the emissions of the covered manure compared to the control when 5 cm of clay was used as fresh dairy manure cover in a field trial [12]. Only when a thicker LECA® cover corresponds to a 14 cm layer, a significant reduction of ammonia volatilization was observed [13]. For a thinner cover of 7 cm, a reduction of 16.81% compared to the control was assessed but was not defined as significant [18]. A LECA® surface layer depth of 2 cm reduced $NH_3$ emissions by 21% when applied to stored liquid manure [35]. According to Nartey et al. [12] even when the LECA® cover forms a firm surface crust, the gaps between the granules allow $NH_3$ volatilization making the superficial cover application ineffective.

Lastly, NC showed emissions ranging from 7.8 $g\ m^2\ h^{-1}$ to 2.4. On the second day, the maximum emissions started to decrease not maintaining a stable trend. From day 13 a superficial floating crust started to form in all the replicates. The crust was nonhomogeneous and cracked very easily but did not sink. The minimum temperature between all the tested groups was registered in NC and accounts for 17.1 °C. Ammonia reduction efficiency and the emission pattern appeared to be consistent throughout the trial. Emission of $NH_3$ (EF) as a percentage of nitrogen emitted compared to the total nitrogen present at the beginning of the storage ranged from 0.18 to 0.61 (Table 5). The lowest emission factor was registered in B, the highest in L, showing the effectiveness of the biochar cover in reducing ammonia emission.

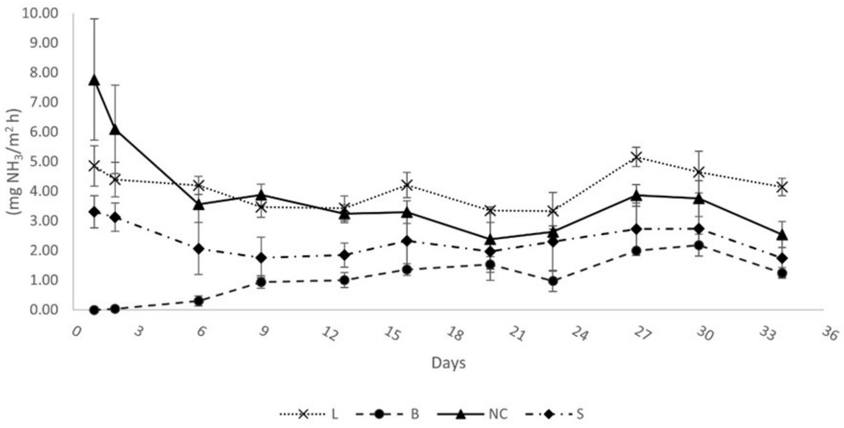

**Figure 2.** Daily ammonia emission measured during the trial. Error bars indicate SEM.

**Table 5.** Emission factors (EFs) referred to TKN and TAN calculated after 34 days of storage. NH3 emissions reduction efficiency (RE %) of the tested cover compared to the control. Values refer to 24 hours, 9 days, 34 days of measurement. Negative values indicate an enhancement of ammonia emissions.

| | EF (%) | | RE (%) | | |
|---|---|---|---|---|---|
| | **TKN** | **TAN** | **24 hours** | **9 days** | **34 days** |
| **NC** | 0.54 | 1.15 | - | - | - |
| **B** | 0.18 | 0.38 | 100±0.0 | 93±0.02 | 67±0.06 |
| **S** | 0.35 | 0.74 | 52±0.07 | 49±0.07 | 36±0.17 |
| **L** | 0.61 | 1.29 | 33±0.02 | 10±0.01 | -13±0.22 |

Ammonia reduction efficiency and the emission pattern appeared to be consistent throughout the trial. Emission of $NH_3$ (EF) as a percentage of nitrogen emitted compared to the total nitrogen present at the beginning of the storage ranged from 0.18 to 0.61 (**Table 5**). The lowest emission factor was registered in B, the highest in L, showing the effectiveness of the biochar cover in reducing ammonia emission.

Ammonia reduction efficiency (RE) during the trial and among the treatments are shown in Table 5. The measured RE highlight how B had emissions close to 0 for the entire first duration of the trial while L during the same period had almost lost the mitigation effect. Definitely, L at the end of the trial showed a negative RE.

### *3.3. Comparative Cost of Natural Covers*

Given the trend equation shown in Figure 3, the cover thicknesses determined, considering a storage tank with an emitting surface of 700m2 and the targeted RE, in RE50 were 1.8 cm, 13.2 cm, 9.8 cm, for biochar, LECA® and straw, respectively. The relative volumes required to cover the storage tank with the calculated cover layer were 12.4 m3, 92.2 m3, 68.3 m3 for biochar, LECA® and straw, respectively. The cover thicknesses for RE70 were 3.2 cm, 15.5 cm, 12.1 cm with corresponding required volumes of 22.7 m3, 107.9 m3, 84.8 m3 for biochar, LECA® and straw, respectively. In order to assess the economic impact, the unit price of biochar, including transport costs, was set at 500 €/m3 as indicated by the seller from whom the biochar was purchased. According to available online sources, the price range for LECA® is between €8 and €10 for 50 litres, while straw costs between €150 and €170 per tonne. The total cost of covering a 700 m2 storage tank with the selected materials is 6191 €, 16602 €, 6146 € in RE50 and 11366 €, 19420 €, 7634 € in RE70 for biochar, LECA® and straw respectively. These results are reported in Table 6.

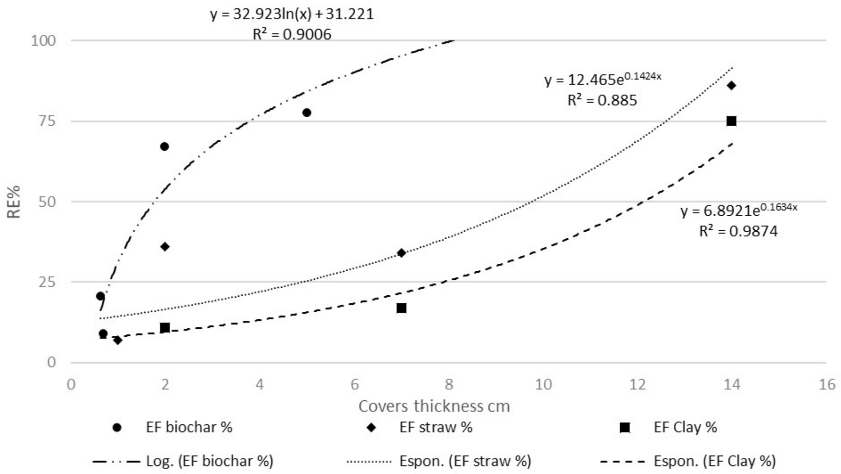

**Figure 3**. Reduction efficiency (RE) of ammonia, related to the thickness of the cover (cm) applied on the manure surface.

**Table 6.** Cover layer thickness, required volume, and total cost for different materials at two target ammonia reduction efficiencies (RE 50% and RE 70%) for a 700 m² storage tank.

| Material | RE target (%) | Cover thickness (cm) | Required volume (m³) | Total cost (€) |
|---|---|---|---|---|
| **Biochar** | 50 | 1.8 | 12.4 | 6191 |
| | 70 | 3.2 | 22.7 | 11366 |
| **LECA®** | 50 | 13.2 | 92.2 | 16602 |
| | 70 | 15.5 | 107.9 | 19420 |
| **Straw** | 50 | 9.8 | 68.3 | 6146 |
| | 70 | 12.1 | 84.8 | 7634 |

As shown in Figure 3, the RE of biochar increases rapidly with a small increase of the cover thickness, following a logarithmic trend line. On the other hand, straw and LECA® follow an exponential trend line. The main difference between the exponential and logarithmic growth models is that the logarithmic growth model is suitable for data that increases rapidly in the beginning and then levels off over time. This shows how the RE of the LECA® and straw coverings increases slowly with low thickness. On the contrary, at lower thicknesses biochar is more effective in reducing ammonia emissions compared to the other materials. This may be due to the fact that biochar acts not only as a physical barrier, but its chemical and physical properties enhance its performances. Therefore, LECA® and straw require a thicker cover compared to biochar to achieve the same RE at lower thicknesses, whereas at lower thicknesses biochar is more effective in reducing ammonia emissions. This may be due to biochar acting not only as a physical barrier, but also through its chemical and physical properties that enhance its performance. Therefore, LECA® and straw require a thicker cover to achieve the same RE, confirming that biochar is more effective at lower cover thicknesses. These price considerations provide a comprehensive view of the financial aspects associated with the use of these cover materials, considering only material and transport costs. A full cost analysis would also include storage, manpower, energy, frequency of cover application, and related costs [45].

For straw, transport can be difficult and its availability varies seasonally. High price and transport costs are not always assumed; for example, a study on orchard waste conversion into biochar shows that the feedstock could be collected for free [32]. In some cases, farmers pay to have their waste biomass collected. The type of biomass stream affects both biochar yield and density [22] which also applies when biochar is produced from livestock manure [46].

### *3.4. Limitations of the Study and Future Work*

Despite the encouraging outcomes observed in controlled laboratory settings, it is important to acknowledge several limitations when interpreting the findings of this study. The experimental duration of 35 days is comparatively brief when set against typical on-farm storage times, which may extend over several months. Consequently, the long-term stability and persistence of the mitigation effect remain uncertain. Furthermore, the experimental setup failed to replicate certain environmental dynamics that occur under real farm conditions. Factors such as wind, rainfall, temperature fluctuations, and the periodic addition of fresh slurry to the storage tank can significantly influence the cover integrity and ammonia volatilisation rates. These variables have the potential to modify the physical composition of the cover materials, particularly lightweight ones such as straw and biochar, thereby impacting their efficiency over time. Furthermore, it is important to note that the test conditions may not fully represent the variability in digestate composition that occurs in practice. This is due to the fact that differences in feedstock, anaerobic digestion process, and storage management can influence ammonia emissions. The uniform layer thickness of 2 cm, which was utilised for all materials in this study, was selected for the purpose of comparative analysis. However, it is acknowledged that this thickness may not align with the optimal operational thickness under field conditions. It is recommended that future research efforts concentrate on the execution of full-scale trials. The objective of these trials should be to evaluate the performance, durability, and management requirements of biochar and other floating covers under variable climatic and operational conditions.

## 5. Conclusions

The utilization of mitigation strategies to minimize $NH_3$ emissions during liquid digestate storage has become fundamental. The application of floating cover has been assessed to be an efficient mitigation method. In this study, three cover materials were compared, biochar, clay LECA®, and straw. From the outcome of our investigation, it is possible to conclude that in a controlled environment, biochar is the most effective cover material. The highest mitigation effect was registered when the biochar was used as cover, showing an overall reduction of cumulative emissions of 67%. Other results obtained suggest that to have proper reduction in terms of ammonia mitigation when using LECA® cover a thin layer is not sufficient, causing in this study an enhancement of the ammonia volatilization compared to the control. Clearly, further research will be needed to understand logistics and management aspects. The behaviour of biochar must be studied to better understand how to properly manage a cover when applied under farm scale conditions, in order to assess the effect of wind and rain on biochar mitigation effect. Further studies are also needed to investigate the main physical properties of biochar in relation to the pyrolysis process and how the production techniques can influence gaseous emission mitigations and production costs.

Finally, the findings of our research highlight how biochar options in terms of ammonia abatement were economically favorable compared to other materials as well as the straw. It is worthy of notice that the biochar used in this study is produced from virgin biomass, derived from a gasification process conducted for energy purpose. Thus, in this case biochar is a by-product and its production cost is partially reduced by income derived by energy production, compensating in this way the high cost of the initial material.

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