THE EFFECT OF UNTREATED AND ACIDIFIED BIOCHAR ON NH₃-N EMISSIONS FROM SLURRY DIGESTATE

PAVEL COVALI¹,*, HENN RAAVE¹, JORDI ESCUER-GATIUS¹, ALLAN KASSIK², TÕNU TÕNUTARE¹, ALAR ASTOVER¹

¹ Chair of Soil Science, Institute of Agricultural and Environmental Sciences, Estonian University of Life Sciences, 51006 Tartu, Estonia.
² Chair of Animal Nutrition, Institute of Veterinary Medicine and Animal Sciences, Estonian University of Life Sciences, 51006 Tartu, Estonia.
* Corresponding author: covali@emu.ee

ABSTRACT. The development of new options to reduce ammonia (NH₃) emissions during slurry manure storage is still required due to the shortcomings of the current technologies. This study aimed to identify to what extent untreated and acid-treated biochar (BC), and pure acids could reduce ammonia nitrogen (NH₃-N) volatilization and increase nitrogen retention in slurry digestate. Slurry digestate was amended with untreated BC; BC treated with H₂SO₄, H₃PO₄ or H₂O₂ acids; and pure acids (H₂SO₄, H₃PO₄ or H₂O₂). There were two BC application methods: mixed into the digestate or applied on the surface. H₂SO₄ and H₃PO₄ acids, untreated BC when applied mixed into the digestate and acidified BC treatments applied on the surface of the digestate, effectively reduced the NH₃-N emissions. Acidification increased the specific surface area and number of O-containing surface functional groups of the BC and decreased the pH, alkalinity and the hydrophobic property. Compared to untreated BC, the ability of BC to reduce NH₃-N emissions was greater when it was acidified with H₂SO₄ and applied to the digestate surface. The effect on digestate pH of acidified BC when applied mixed into the digestate was not different, except for H₂O₂, from that of the addition of the respective pure acid to digestate. The total N concentration in digestate was not significantly correlated with NH₃-N emissions. These findings indicate that acidified BC could be an effective conditioner to reduce NH₃-N emissions from slurry digestate storage.

Keywords: biochar, slurry digestate, NH₃-N emissions reduction, biochar acidification, digestate N concentration

1. INTRODUCTION
In recent years, there has been an increase from farming communities in using slurry conditioners. They mitigate NH₃ emissions in a cost-efficient manner (Kavanagh et al., 2019) and are relatively easily applied to manure compared with other technologies that require modifications to the existing infrastructure and/or the purchase of expensive...
equipment (Maurer et al., 2016). Biochar (BC) is a porous material produced through pyrolysis or gasification of biomass at different temperatures with no or very low oxygen (O) availability (Sohi et al., 2009). BC has received increasing attention in recent years because of its diverse functionality in the fields of climate change mitigation, sustainable agriculture and environmental control (Xiao et al., 2018). The BC properties of high surface area, high porosity and high cation or anion exchange capacity make it a promising slurry conditioner to enhance NH$_4^+$ retention (Li et al., 2018) and reduce nitrate (NO$_3^-$) leaching (Saarnio et al., 2018). BC has been shown to decrease NH$_3$ volatilization and improve N retention in poultry litter composting (Agyarko-Mintah et al., 2017) and to adsorb ammonium nitrogen (NH$_4^+$-N) from piggery manure anaerobic digestate slurry (Kizito et al., 2015), thus enhancing the fertilizer value of manure. However, with the increasing quantity of BC addition, the alkalinity of BC is likely to increase the pH of the manure and shift the NH$_4^+$/NH$_3$ equilibrium toward NH$_3$ volatilization (Sun et al., 2019). To address this issue, the acidic oxidation of BC can neutralize the alkaline pH and facilitate the adsorption of NH$_4^+$ because of the increased amount of O-containing surface functional groups (Sajjadi et al., 2019). Maurer et al., (2017) determined that untreated BC can effectively mitigate NH$_3$ emissions from stored swine manure. At the same time, Peiris et al., (2019) stated that acid modification can affect the physicochemical properties of the BC which in turn could alter the mitigation effect.

The aim of the present study was to investigate: (i) the ability of hay BC to reduce NH$_3$-N emissions from digestate; (ii) to what extent the suppression effect of NH$_3$-N emissions of BC can be enhanced through acidification; (iii) which method is more effective for the application of untreated and acidified BC (mixed or surface), and (iv) whether untreated and acidified BC addition reduces total N (N$_{tot}$), NH$_4^+$-N and nitrate-nitrogen (NO$_3^-$-N) losses in digestate.

2. MATERIALS AND METHODS

2.1. Experimental design

The trial was carried out under controlled laboratory conditions at the Estonian University of Life Sciences (EULS) during a period of 240 days from October 2018 until May 2019. The experiment included a total of 12 treatments and consisted of two experimental factors: (i) digestate conditioner (untreated BC, acidified BC and acid) and (ii) application method of digestate conditioner (BC on the surface – BCs; BC mixed into the digestate – BCm). The pure acids were applied in pure form mixed into digestate only (Table 1).

Table 1. Experimental treatment abbreviations and description.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Treatment description</th>
</tr>
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<tbody>
<tr>
<td>Control</td>
<td>Digestate</td>
</tr>
<tr>
<td>BCm</td>
<td>Untreated BC mixed into digestate</td>
</tr>
<tr>
<td>BCs</td>
<td>Untreated BC on the digestate surface</td>
</tr>
<tr>
<td>BCm + H$_2$SO$_4$</td>
<td>BC treated with sulfuric acid mixed into digestate</td>
</tr>
<tr>
<td>BCs + H$_2$SO$_4$</td>
<td>BC treated with sulfuric acid on the digestate surface</td>
</tr>
<tr>
<td>BCm + H$_3$PO$_4$</td>
<td>BC treated with phosphoric acid mixed into digestate</td>
</tr>
<tr>
<td>BCs + H$_3$PO$_4$</td>
<td>BC treated with phosphoric acid on the digestate surface</td>
</tr>
<tr>
<td>Formula</td>
<td>Description</td>
</tr>
<tr>
<td>-------------------------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>BCm + H₂O₂</td>
<td>BC treated with hydrogen peroxide mixed into digestate</td>
</tr>
<tr>
<td>BCs + H₂O₂</td>
<td>BC treated with hydrogen peroxide on the digestate surface</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>Sulfuric acid mixed into digestate</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>Phosphoric acid mixed into digestate</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>Hydrogen peroxide mixed into digestate</td>
</tr>
</tbody>
</table>

For accuracy and logistical reasons, the experiment was conducted in two batches. In the first batch, NH₃ emissions and digestate pH were measured and replicated three times from October 2018 until May 2019. In parallel, the second batch examined NH₄⁺-N, NO₃⁻-N, total nitrogen (Nₜot) and total carbon (Cₜot) concentrations, which were replicated four times from February 2019 until April 2019. In both batches, the replications were carried out in the same order and the digestate conditioners were applied in the same amounts, manner and laboratory conditions.

### 2.2. Materials

The BC was produced from reed canary (*Phalaris arundinacea* L.) hay pellets and torrefied at 300 °C. The quantities on a dry weight basis of total phosphorous (Pₜot), total potassium (Kₜot), total calcium (Caₜot) and total magnesium (Mgₜot) were 2400 mg kg⁻¹, 22,800 mg kg⁻¹, 9300 mg kg⁻¹ and 4700 mg kg⁻¹, respectively. The ash concentration was 10.4%, cumulative pore volume represented 0.0015 cm³ g⁻¹, and the concentration of volatile compounds was 62.9%. Physicochemical details of the acidified BC conditioners are shown in Table 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Digestate</th>
<th>BC</th>
<th>BC + H₂SO₄</th>
<th>BC + H₃PO₄</th>
<th>BC + H₂O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.2</td>
<td>6.40</td>
<td>1.55</td>
<td>2.65</td>
<td>4.80</td>
</tr>
<tr>
<td>Specific surface area, m² g⁻¹</td>
<td>-</td>
<td>126.14</td>
<td>161.48</td>
<td>145.92</td>
<td>166.31</td>
</tr>
<tr>
<td>Acid neutralization capacity (CaCO₃, %)</td>
<td>-</td>
<td>3.80</td>
<td>0.00</td>
<td>0.49</td>
<td>3.86</td>
</tr>
<tr>
<td>Dry matter (%)</td>
<td>4.06</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Cₜot (%)</td>
<td>40.37</td>
<td>50.29</td>
<td>51.18</td>
<td>53.57</td>
<td>51.77</td>
</tr>
<tr>
<td>Nₜot (%)</td>
<td>6.87</td>
<td>2.79</td>
<td>2.81</td>
<td>2.96</td>
<td>2.85</td>
</tr>
<tr>
<td>C/N</td>
<td>5.88</td>
<td>18.03</td>
<td>18.22</td>
<td>18.10</td>
<td>18.16</td>
</tr>
<tr>
<td>NH₄⁺-N (mg kg⁻¹)</td>
<td>46 390</td>
<td>80</td>
<td>400</td>
<td>230</td>
<td>220</td>
</tr>
<tr>
<td>NO₃⁻-N (mg kg⁻¹)</td>
<td>3 520</td>
<td>60</td>
<td>80</td>
<td>90</td>
<td>80</td>
</tr>
</tbody>
</table>

### 2.3. Experimental set-up

A multi-gas detection equipment X-am 7000 (Dräger, Lubeck, Germany) connected to an 860-CG acrylic desiccator chamber with a gas port (Plas-Labs, Lansing, MI, USA) was used to measure NH₃ concentrations. A schematic of the experimental set-up is shown in Figure 1.
2.4. Measurements and analyses

2.4.1. NH₃ concentration and digestate pH
The NH₃ concentrations were measured in two separate sessions. The first session lasted for 48 h (2880 min), immediately after the digestate was exposed to ambient conditions. In the second session, the gas concentrations were monitored for 24 h (1440 min) from the 7th to 8th day after the beginning of the experiment. The pH of the digestate was measured with an HD 2156.2 pH meter (Delta OHM, Padua, Italy) at the beginning of the experiment and after 48, 72, 96 and 120 h. In the untreated and acidified BCs treatments, the pH measurements were recorded under the BC layer (approximately 3–5 cm deep) and in the middle of the vessel (approximately 7–9 cm deep). In the untreated and acidified BCm as well as in the control and acid treatments, the pH was measured only in the middle of the vessel.

2.4.2. Nutrient concentration
The N₉tot, C₉tot, NH₄⁺-N and NO₃⁻-N concentrations were measured in the digestate at the beginning of the experiment and after 30 days. The N₉tot and C₉tot concentrations were determined after dry combustion with a varioMAX CNS elemental analyzer (Elementar Analysensysteme GmbH, Langenselbold, Germany). The NH₄⁺-N and NO₃⁻-N were determined after steam distillation (Bremner and Keeney, 1965) using a UDK 126D distillation unit (VELP Scientifica, Usmate Velate, Italy). The N-containing species were calculated by subtracting the concentration in the BC from the total concentration retained in the digestate.

2.5. Statistical analysis
Statistical analysis was conducted using the R programming software (R Development Core Team, 2019). Data were analyzed using analysis of variance (ANOVA) to study the effect of BC treatment (untreated and acidified), time and the interaction between them on NH₃ emissions. When significant differences existed, a post-hoc Tukey’s honest
significant difference (HSD) test was conducted to study the differences between groups (Tukey, 1977). The different N compounds were tested between treatments at the end of the 30-day period. Linear regression and Pearson correlation coefficient were used to analyze the relationship between NH$_3$-N emissions and pH or mineral N concentration.

3. RESULTS AND DISCUSSION

3.1. Effect of untreated BC on NH$_3$-N emissions

The suppression effect of untreated BCs was not different from untreated BCm during the first 3.5 h (p = 0.80). In the untreated BCm treatment, a sharp increase in NH$_3$-N emissions was detected during the first 1.5 h (Figure 2B), which was followed by a decrease between 1.5 and 3.5 h. However, in untreated BCs, no emissions were recorded during the first 1.5 h, and a steep increase in NH$_3$-N emissions was recorded from 1.5 until 3.5 h. From 3.5 h onward, the NH$_3$-N emissions in untreated BCs were higher than untreated BCm, but the differences were not significant (p > 0.05).

![Figure 2. NH$_3$-N emissions (mean ± standard error) during 0–48 h and from the 7th to 8th day after the application of pure acids (A), untreated and acidified BC mixed in the digestate (B) and untreated and acidified BC applied on the digestate surface (C). Control without conditioner.](image-url)
The short-term effectiveness (<1.5 h) of untreated BCs is likely to be related to the formation of a physical barrier on the digestate surface. The physical cover of untreated BCs particles prevented the digestate from being exposed to the surrounding environment and slowed down the transfer of NH3-N gases at the digestate–air interface. The effectiveness of untreated BCs declined after 1.5 h possibly due to its strong water repellent characteristic. The hydrophobic property prevented the BCs particles from submerging deeper into the digestate, and the resulting BC cover was less resistant to NH3-N emissions. This strong physical property was probably induced by the large quantity of aliphatic functional groups on the BC surface (Figure 3). Previous studies have shown a strong correlation between hydrophobicity and the presence of aliphatic functional groups (–C-H, CH2) on the BC surface (Kinney et al., 2012; Mao et al., 2019). Our findings are in accordance with those of Holly and Larson (2017) in which BC, made from wood and maize cob pyrolyzed at 400 °C, effectively mitigated NH3-N emissions from the dairy manure storage. The effectiveness of BC in their experiment was due to the action of the physical barrier on the manure surface provided by the BC cover thickness of 3.1 and 2.5 cm.

NH3-N volatilization in BCm treatment occurred probably because of the pH increase in the digestate caused by aeration when the BC was mixed with the digestate. In the BCs treatment, the NH3-N emissions and pH under the BC cover were notably lower than in control because the digestate was not in direct contact with ambient air. The reduced effect of the BCs treatment might also be because the relative change of digestate pH only occurred below the BC cover. According to García-González et al. (2015), manure aeration stimulates OH− groups release and increases manure pH, which in turn increases the conversion rate of NH4+-N to NH3-N. In the BCm treatment, however, the aeration increased NH3-N emissions in the short-term (<3.5 h). As the BCm particles started to migrate to the upper part of the vessel, they formed, like the BCs treatment, a physical barrier against NH3 loss. However, not all BCm particles floated to the digestate surface after mixing to provide resistance to NH3-N emissions. The BCm particles located closer to the center of the vessel decreased the digestate pH in the middle of the vessel and diminished the formation of NH3-N. The pH reduction was furthermore exacerbated by greater contact between BCm particles and digestate.

### 3.2. Effect of acidification on BC characteristics and NH3-N emissions

BC acidification improved the suppression effect of BCs but not of BCm (Figure 2B,C). Acidification with H2SO4, H2O2 and H3PO4 prolonged the reduction effect of BCs by 41.5, 38.5 and 31.5 h, respectively.

Of the pure acids, only H2SO4 and H3PO4 significantly reduced NH3-N emissions. During the 48-h time period, the reduction effect of both acids was statistically significant during the first 5 h and from 28 to 33 h (p < 0.01) (Figure 2A).

The physicochemical characteristics of BC that affected NH3-N emissions were positively influenced by acidification. SSA increased the most in BC+H2O2 and BC+H2SO4, whereas the SSA increase was slightly less in BC+H3PO4. Maximum peaks of hydroxyl (–OH) and carbonyl (–C=O) functional groups were observed in the BC+H2SO4. The peak of aliphatic
The amount of previously mentioned functional groups was a little lower in BC+H$_2$O$_2$. Vithanage et al. (2015) and Cibati et al. (2017) showed that BC treatment with H$_2$SO$_4$ increased the O/C ratio twofold, whereas treatment with H$_2$O$_2$ only increased it 1.5-fold.

Figure 3. FTIR spectra of untreated and acidified BC with identified functional groups.
These findings indicate the capacity of different acids to generate O-containing functional groups on the BC surface (Shi et al., 2019). The addition of O-H, C=O, C-O and N-H functional groups on the BC surface can decrease its hydrophobicity (Ahmed et al., 2016; Rechberger et al., 2017). Shen et al. (2008) found that acid treatment of BC with HNO₃ and H₂SO₄ enhanced the hydrophilic surface of the BC. This means that BC acidification is an effective method to cause the hydrophobic surface of the BC to become slightly more hydrophilic. Acidification remarkably reduced the pH and alkalinity of BC. The effect of acid-treated BC on digestate pH was comparable, except for H₂O₂, to the respective pure acid applied to the digestate alone. Our results contrast with those of Huff and Lee (2016), who found that the pH of BC was only slightly reduced by H₂O₂ because of the weak ability of this acid to create acidic functional groups on the BC surface.

Acidification improved the effect of BCs to suppress NH₃-N emissions. As a result of the developed hydrophilic property, acidified BC particles could form a thicker cover on the digestate surface that withstood the pressure exerted by the gases in the digestate for a longer period than untreated BCs. The ability to reduce NH₃-N emissions of BCs+H₂SO₄ or BCs+H₃PO₄ was slightly greater than that of both acids when applied in the pure form in the first 48 h only (Figure A2).

However, the capacity of BCm to reduce NH₃-N emissions was not improved by acidification because most of acidified BCm particles could not float to the digestate surface as they did in the untreated BCm treatment. Although the effect of acidified BCm to influence digestate pH was comparable to that of the pure acids, their impact on NH₃-N emissions was smaller than that of the pure acids. Such results might be because of the slower capacity of acidified BCm to alter the digestate pH suggested mostly by the great differences in pH and NH₃-N emissions between acid and acidified BC treatments observed in the early stage of the experiment (<3.5 h) (Figure 2A,B). The NH₃-N emission difference later diminished when digestate pH in acidified BC and acid treatments leveled off. The results of the current study show that the effect of acidified BC on digestate pH remained the same as that of pure acid for at least five days. The pH of digestate where acidified BC was added could increase at a certain moment in time due to the salts present in the ash of acidified BC. Thus, further studies are needed to analyze the effect on pH in longer periods.

### 3.3. Effect of conditioner treatments on N concentration in digestate

Thirty days from the beginning of the experiment, the NH₄⁺-N concentration was significantly higher \( (p < 0.01) \) than that of the control in all conditioner treatments, except H₂O₂. NO₃⁻-N concentration was higher than control in the BC+H₂O₂, BC+H₂SO₄ and the H₂SO₄ and H₃PO₄ treatments \( (p < 0.001) \) and N₄tot in the H₂SO₄ and H₃PO₄ treatments only \( (p < 0.01) \) (Figure 4).

The N₄tot concentration in digestate was not significantly correlated with NH₃-N emissions recorded in the first 48 h and between the 7th and 8th days. In addition to NH₃-N emissions, the N₄tot concentration could be affected by other N-containing gas emissions. Previously, Chadwick et al. (2011) showed that the crust or permeable cover formed on the slurry surface during the storage period reduced NH₃ but increased N₂O emissions. In
addition, in our experiment, the BC cover might have stimulated N$_2$O emissions because of the anaerobic conditions.

**Figure 4.** Concentration of NH$_4^+$-N, NO$_3^-$-N and N$_{tot}$ (mean ± standard error; n = 3) in the digestate 30 days after conditioner addition.

The conditioners used in the current experiment affected digestate pH and probably also gaseous exchange at the liquid–air interface by the cover formed on the digestate surface. As digestate pH increases, the concomitant increase of NH$_3$ concentration may inhibit the activity of nitrifying bacteria. As a result, NH$_4^+$ is converted into N$_2$O and dinitrogen (N$_2$) gases bypassing the NO$_3^-$-N phase (Soliman and Eldyasti, 2018).

In the BCs treatments, N$_2$O emissions were probably not the main factor influencing the NO$_3^-$-N concentration in digestate. The NO$_3^-$-N concentration was higher in acidified BCs than in untreated BCs, even though a longer-lasting acidified BCs cover and slightly lower digestate pH should promote denitrifying bacteria activity (Chadwick et al., 2011; Kupper et al., 2020; Šimek et al., 2002). It is possible that NO$_3^-$-N was adsorbed by acid-treated BC, and its degradation by microorganisms became more difficult. Lan et al. (2017) noted that BC adsorption of NO$_3^-$ in soil can decrease its availability for denitrifiers. The NO$_3^-$-N
concentration between acidified BCs and BCm with $\text{H}_2\text{SO}_4$ or $\text{H}_2\text{O}_2$ was not different, although the cover was not formed in acidified BCm. NO$_3^-$ sorption could be promoted by surface basic functional groups such as primary and secondary amine groups (Figure 3) via electrostatic interactions. This is in accordance with the findings of Wu et al. (2019) that NO$_3^-$ can interact with amine groups through electrostatic interactions during the adsorption process. In BC+H$_3$PO$_4$, the NO$_3^-$ could be limited because of the presence of competitive phosphate anions (PO$_4^{3-}$) bound by sorption sites during acidification, which could remain immobilized because of their highly negative charge. A small amount of NO$_3^-$ could be adsorbed to positively charged cations (K$^+$, Ca$^{2+}$ and Mg$^{2+}$) present in the ash of acidified BC by bridge bonding. Fidel et al. (2018) mentioned that some NO$_3^-$ sorption to acidified BC can occur via cation bridging. However, NO$_3^-$ could not be bound by untreated BC primarily because of the lower peaks of basic functional groups. Alsewaileh et al. (2019) found that low-temperature BC (300 °C) exhibited minimal adsorption efficiency of NO$_3^-$ because of the reduced total basicity (surface basic functional groups) and limited surface area.

4. CONCLUSION
In this study, $\text{H}_2\text{SO}_4$ and $\text{H}_3\text{PO}_4$ acids, untreated BCm and acidified BCs treatments were found in reducing NH$_3$-N emissions from digestate. Acids reduced the digestate pH and reduced the rate of conversion from NH$_4^+$-N to NH$_3$-N. Untreated BCm formed a physical barrier on the digestate surface that isolated the digestate from the atmosphere. Acidification of BC increased its specific surface area and number of O-containing surface functional groups and decreased the pH, alkalinity and the hydrophobic property. The impact on NH$_3$-N emissions of acidified BC was dependent on the application method. Compared with untreated BC, the ability of BC to reduce NH$_3$-N emissions was greater when it was acidified with $\text{H}_2\text{SO}_4$ and applied to the digestate surface. The novel finding of our study is that acidified BC applied on digestate surface could have an effective application potential to reduce NH$_3$ emissions from slurry storage tanks.

Our results suggest also that BC cover might stimulate N$_2$O emissions because of the anaerobic conditions. In addition, BC+H$_2$SO$_4$ and BC+H$_2$O$_2$ might adsorb NO$_3^-$-N present in digestate and decrease its availability to denitrifying bacteria. These new hypotheses need to be tested in future research.
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APPENDIX A

Figure A1. Cumulative NH₃-N emissions for 0–48 h from conditioner application (mean ± standard error (n = 3). Results marked with different lowercase letters are statistically different.

Figure A2. NH₃-N emissions from pure acids, untreated and acidified BCm treatments depending on digestate pH (n = 3).
APPENDIX B

On the first page of the paper, just below the list of authors and their address, indicate the general paper number CSBE21XXX – followed by the appropriate Conference or Symposium name (if apply). Choose among the following:

4th international Symposium on Gas Emissions and Dust from Livestock (EMILI)

World Congress on Computers in Agriculture 2021 (WCCA)

9TH INTERNATIONAL SYMPOSIUM ON CEMENT BASED MATERIALS FOR A SUSTAINABLE AGRICULTURE (CSA)