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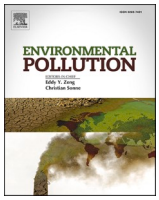

The effect of biochar and acid activated biochar on ammonia emissions during manure storage

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ABSTRACT

Animal manure contains valuable plant nutrients which need to be stored until field application. A significant proportion of slurry nitrogen is volatilized in the form of ammonia (NH_3) during storage. This impacts human health, biodiversity, air and water quality and thus urgent action is needed to reduce NH_3 emissions. In this experiment, we evaluated the NH_3 emission mitigation potential of biochars derived from miscanthus (MB) and solid separated anaerobic digestate (DB), and orthophosphoric acid activated MB (AMB) and DB (ADB) as well as lightweight expanded clay aggregate (LECA) during four months of liquid manure storage. A slurry without amendment was included as a control (Ctrl). Acid activated and non-activated biochars were applied on top of the slurry maintaining a 7 mm thick surface layer, while LECA was applied in a 2 cm thick layer. NH_3 emissions were measured by photoacoustic analyzer. In comparison to Ctrl, acid activated biochar decreased ($p < 0.05$) NH_3 emissions during the slurry storage. Activated biochar reduced the emissions by 37–51% within the first month of slurry storage and achieved a 25–28% emissions reduction efficiency throughout the four month period due to the reduction in emission mitigation efficiency as the storage period progressed. LECA reduced NH_3 emissions by 21% during storage. Losses of NH_3 as a percentage of total ammoniacal N were 29–31% for activated biochars, 35–39% for non-activated biochars and 33% for LECA. In conclusion, acid activated biochars and LECA could be good floating-covers to mitigate NH_3 emissions during manure storage, but activated biochars may have better mitigation potential than LECA.

1. Introduction

Continuous growth in the global demand for animal products is driven by the increase in income and population growth that require large-scale animal production (FAO, 2022). Animal production generates faeces and urine which is a valuable source of plant nutrients and needs to be stored for land spreading. Storage of manure is a major source of ammonia (NH_3) emission which impacts human health by formation of fine particulate matter ($PM_{2.5}$), biodiversity, and air and water quality (de Vries, 2021). The United Kingdom (UK) has international commitments to reduce NH_3 emissions by 16% by 2030, based on 2005 levels (DAERA, 2022). Northern Ireland (NI) is responsible for 12% of UK NH_3 emissions, despite the fact NI has only 3% of the UK population and 6% of the land area, and these emissions increased by almost 19% between 2009 and 2019 due to increasing livestock numbers, indoor housing systems and insufficient NH_3 emission reduction technology adoption (DAERA, 2022).

Various practices have been implemented to minimize NH_3 emission reduction from slurry storage such as slurry acidification (Kavanagh et al., 2019; Misselbrook et al., 2016; Petersen et al., 2016), use of light expanded clay aggregates (LECA) (Misselbrook et al., 2016; Nartey et al., 2021), biochar addition (Covali et al., 2021; Dougherty et al., 2017; Hung et al., 2022) etc. Biochar is produced by thermochemical transformation of biomass in the absence of oxygen, i.e., pyrolysis. Biochar is considered as a potential option to reduce NH_3 emissions during slurry storage by either using it as a slurry cover (Covali et al., 2021; Dougherty et al., 2017; McGuiggan et al., 2022) or mixing it with slurry (Hung et al., 2022; Liu et al., 2021; Pereira et al., 2020) with the additional advantages of building soil health, improving soil physical and chemical properties, carbon sequestration, reducing GHG emissions and increasing crop productivity after field application (Antonangelo et al., 2021; Xu et al., 2021). The covering of the slurry store surface with biochar or LECA is envisioned to offer resistance to transfer of NH_3 from the slurry surface to the atmosphere and thus reduce NH_3 emissions (Holly and Larson, 2017; Sommer, 1997).

Biochar has unique properties such as being porous in nature giving

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it a large surface area to volume ratio and having polar oxygenated functional groups that help to adsorb slurry-derived NH_3 during storage (Sajjadi et al., 2019). Surface functional groups of biochar provide a favourable site to adsorb NH_3 while porosity and surface area are effective for ammonium ion (NH_4^+) adsorption thereby reducing NH_3 emissions (Feng et al., 2021; Wang et al., 2016). The physical properties and functional groups can be modified by chemical activation (Sajjadi et al., 2019). Acid activation drastically increases biochar surface area, pore volume and functional groups (Trinh et al., 2020). With acid activation of biochar after pyrolysis, the acid quickly diffuses to the outer part of the particles and dissociates weakly bonded components (Sun et al., 2015). At the same time, it creates new functional groups inside the pores and on the surface and develops negatively charged surface areas (Tsang et al., 2007). A strong negative charge on the surface may adsorb more positive ions such as NH_4^+ and reduce the NH_3 emission.

Several studies have been conducted regarding the use of biochar as a bio-cover or bio-mix to reduce NH_3 emissions. However, these studies have shown variable effectiveness for reducing NH_3 emissions. For example, Covali et al. (2021) found a 48% reduction of NH_3 in a 2 day incubation experiment. Häni et al. (2012) observed a 25% emission reduction with biochar over a 20 day experimental period. Meiirkhanuly et al. (2020) found a 16–25% reduction in NH_3 emissions in a three-week period with the application of biochar, but the efficiency was highest in the first week and gradually reduced over the storage period. In addition, McGuiggan et al. (2022) and Maurer et al. (2017) did not find any reductions in NH_3 emissions with biochar in comparison to unamended slurry, while Liu et al. (2021) observed an increase in the emissions with biochar. Similar to biochar, LECA may be used as a floating cover to reduce the NH_3 emission, but the information is limited and the results are not consistent (Misselbrook et al., 2016; Nartey et al., 2021). The experimental evidence suggests that more information is needed to draw a conclusion regarding effectiveness of biochar and LECA as a floating-cover to mitigate NH_3 emissions and also raise the question: are biochar and LECA effective at mitigating the NH_3 emissions from a cattle slurry store over a typical four-month storage period for the UK and Ireland?

In this study, biochar derived from miscanthus and a solid fraction of anaerobic digestate, and LECA were used as a floating cover. In addition, miscanthus and digestate biochar activated by orthophosphoric acid were also used. The objective of the experiment was to evaluate the effectiveness of these materials for NH_3 emission reduction during four months of slurry storage.

2. Methodology

2.1. Experimental setup and measurements

The slurry storage experiment was conducted from the 5th Jan to the 28th Apr 2022. Experimental treatments were: Control (Ctrl), miscanthus biochar (MB), activated miscanthus biochar (AMB), digestate biochar (DB), activated digestate biochar (ADB), and lightweight expanded clay aggregate (LECA). The six treatments with three replicates were assigned randomly into three blocks during the experiment and thus there were 18 containers in total. The experiment was carried out in an open farm building to simulate the outdoor storage condition.

The slurry used in this experiment was fresh slurry (two days old) collected from the dairy cattle house of the Hillsborough Research Farm, Agri-Food and Biosciences Institute (AFBI), Northern Ireland, UK. The cattle house has in-house storage tanks below the solid floor where manure and urine are collected everyday with scrapping. Prior to the collection, the slurry in the storage tank was mixed with a tractor-driven slurry agitator. Subsequently, slurry was pumped into a slurry tanker equipped with mixing devices and transported to the experimental site.

Digestate solid fraction of anaerobic digestate produced from the AFBI-Hillsborough anaerobic digester was separated by mechanical Screw Press (FAN PSS 3.2780). The anaerobic digester is a continually stirred tank reactor plant consisting of two 650 m^3 digestion tanks where a mixture of dairy cattle slurry and grass silage were used as feedstock. Each tank had a hydraulic retention time of 28 days in series. The primary digester was maintained at 39 °C while the secondary tank was unheated. The separated solid digestate was dried to a moisture content of 15% and subsequently pelleted by a commercial pellet company (Straw Chip Limited, Kildare, Ireland) giving a final moisture content of 12%. Commercially available miscanthus pellets were procured from Agripellets Ltd, Alcester, UK. Digestate and miscanthus pellets were pyrolysed using a Biomacon C100–F Pyrolysis Boiler (R&S Biomass Equipment Ltd, Newtownstewart, NI) at a feed rate of 21 kg h^{-1} and pyrolysis chamber temperature of 675 ± 5 °C.

The containers of 37 L capacity were filled with 20 L of fresh cattle slurry. On top of the slurry, biochar and acid activated biochar (<2 mm size) were spread uniformly maintaining 7 mm depth. The activated biochar was activated by orthophosphoric acid (5% H_3PO_4). During activation, biochar was added to H_3PO_4 solution at 1:2 (w/v) ratio and stirred well to mix. After 5 days of soaking in acid solution, the acid was drained from the biochar using funnels with filter papers of 2.5 μm (Whatman Int. Ltd, England, UK). The activated biochars were dried at 60 °C for 2 days to remove moisture. Grinding of both activated and non-activated dried biochar was performed using a kitchen blender. During grinding, a brief pulse was given 7 times and shaken well every third pulse to avoid over crushing of the biochar near the blades. The biochars were then sieved with a 2 mm sieve to get <2 mm size.

Light expanded clay aggregates (LECA) were granular in nature with a diameter of 10–20 mm and a density of 245 kg m^{-3}, crushing resistance of >0.52 N mm^{-2} and thermal conductivity of 0.095 W mK^{-1}. For LECA the surface layer depth was 2 cm which was lower than reported elsewhere in order to remain comparative to the biochar layer.

2.2. Characteristics of cattle slurry

Slurry properties were characterised before and after the experiment. Slurry dry matter and moisture were determined from drying c. 20 g fresh slurry at 105 °C for 24 h, and then combusted in a muffle furnace at 550 °C to determine ash content. Slurry pH and electrical conductivity (EC) were measured in a mixture of slurry and de-ionized water (1:2.5 w/w) using a HQ series multimeter (HQ4200, Hach Lange Gmbh, Dusseldorf, Germany).

Slurry total N was analysed by the Kjeldahl procedure (The Kjeltec™ 2400 Auto Analyzer, FOSS Analytical, Denmark). For slurry NH_4^+ measurement, 25 g slurry was placed into a 100 mL beaker and quantitatively transferred to a 500 mL volumetric flask by adding/washing with de-ionised water. The suspension was shaken vigorously by hand and poured through a fine sieve. Approximately 100 mL of extract was used for NH_3 analysis using an NH_3 electrode (Orion 9512 NH_3 electrode, Thermo Fisher Scientific Europe, Nijkerk, Netherlands).

2.3. Characteristics of biochar

Biochar properties were analysed by Eurofins Analytic (Eurofins Umwelt Ost GmbH, Germany). Bulk density of biochar was determined by filling 25 mL graduated cylinders with the biochars (<2 mm). The cylinders were tapped a few times during filling to remove the air, compact it and smooth the biochar distribution. The cylinders with biochar were dried at 80 °C for 24 h. Subsequently, the cylinders were tapped for 30 s at the rate of one tap sec^{-1} to compress the biochar in the cylinder prior to weight and volume of the dry biochar being recorded.

Table 1
Cattle slurry properties at the beginning (Before Exp) and at the end of the experiment (After Exp). Ctrl, control (reference slurry); MB, miscanthus biochar; AMB, activated miscanthus biochar; DB; biochar from solid fraction of digestate; ADB, activated digestate biochar; LECA, lightweight expanded clay aggregate. Significant differences at $p < 0.05$ are represented by different letters.

		DM	TN	TAN	pH	Ash
			g kg^{-1} fw			g kg^{-1} dw
Before Exp	Cattle slurry	78.7 ± 0.2 bc	3.9 ± <0.1 a	2.2 ± 0.1 a	8.3 ± <0.1 a	213.2 ± 0.5 cd
After Exp	Ctrl	74.8 ± 3.4 c	3.1 ± 0.1 b	1.9 ± <0.1 b	7.2 ± <0.1 b	240.5 ± 6.0 b
	MB	89.7 ± 4.3 ab	3.3 ± 0.2 b	2.0 ± 0.1 ab	7.1 ± 0.1 b	208.8 ± 3.1 d
	AMB	90.3 ± 5.7 ab	3.4 ± 0.2 b	2.0 ± <0.1 ab	7.1 ± 0.1 b	216.6 ± 3.6 c
	DB	96.3 ± 2.0 a	3.3 ± 0.1 b	2.0 ± 0.1 ab	7.2 ± <0.1 b	267.1 ± 2.4 a
	ADB	94.6 ± 3.8 a	3.4 ± 0.1 b	2.0 ± 0.1 ab	7.1 ± <0.1 b	264.2 ± 4.7 a
	LECA	102.8 ± 52	3.3 ±<0.1 b	2.1 ± <0.1 ab	7.2 ± <0.1 b	689.3 ± 5.6

Note: In DM and Ash analysis, LECA is not included considering the fact that the samples were not representative due to difficulty in sampling.

Table 2
Properties of biochars.

	Unit	Miscanthus	Digestate
BET surface area	m^2/g	308	464
Total C	%	82	55
Total N	%	0.9	1.1
Phosphorus (P_2O_5)	%	6	10
Potassium (K_2O)	%	18	10
Hydrogen	%	0.6	0.5
Sulphur	%	0.2	0.6
Calcium	%	9	17
Iron (Fe_2O_3)	%	2	3
Ash content	%	15	42
Silicon (siO_2)	%	55	37
Conductivity	μS/cm	3420	4760
Calorific value	MJ/kg	20	15

The density of biochar was calculated using the methodology of Ahmedna et al. (1997):

$$Bulk\ density\ (\%) = \frac{Weight\ of\ dry\ biochar\ (g)}{Volume\ of\ dry\ biochar\ (mL)} \times\ 100 \quad (1)$$

Biochar pH was measured using a 5 g air-dried sub-sample as described by Singh et al. (2017). In brief, the subsamples were placed in a 100 mL centrifuge bottle and then 50 mL de-ionized water was added. The suspension was mechanically shaken at 200 rpm for 1 h at 20 °C and the suspension allowed to stand for ~30 min. pH was measured in the suspension using a pH meter (HQ4200 multimeter, Hach Lange Gmbh, Dusseldorf, Germany). The pH electrode was rinsed with de-ionized water and blotted between measurements.

Before stirring of slurry at the end of the experiment, subsamples of the floating biochars and LECA were collected to analyse the ammoniacal N (NH_4^+ and NO_3^-) absorption/adsorption capacity of the materials. During collection, a spoon was used to scrape the surface of the biochar but avoiding the slurry layer disturbances. We added 50 mL of KCl (2 M) to 5 g biochar and the mixture was mechanically shaken for 1 h at 20 °C at 200 rpm. The extracts were filtered via 11 μm filter paper (Whatman Int. Ltd, England, UK) and filtrates were analysed via colorimetry using a continuous segmented flow auto-analyzer (Skalar San^{++}, Breda, Holland). Gravimetric water content (GWC) was determined by drying *c.* 10 g biochar at 105 °C for 24 h.

2.4. Emission measurements

Ammonia emissions measurements started between 10:00–10:30 a.m. using static chamber technique (Liu et al., 2021). During the gas measurement period, the containers were closed with the lids for an hour. The lids were equipped with a butyl rubber septum on top from where a PTFE tube was inserted. One side of the tubes was equipped with a two-way switch valve to regulate the gas flow. During the NH_3 concentration measurements, a photoacoustic analyzer (GASERA F10, Finland) was connected to the container headspace using PTFE tubes and by turning on the switch valve. Prior to gas sampling from containers, three air samples were measured; average of those was NH_3 concentrations at time zero (t_0). Subsequently, three NH_3 measurements were taken from the containers during the closed period, but the first measurement was discarded to avoid carryover effects and thus the average concentration of two measurements were used for the flux calculations. Samples were collected at 17 dates during 4 months of the experimental period, i.e., on day 0, 1, 2, 5, 9, 14, 21, 29, 40, 51, 61, 72, 86, 99, 105, 107, 113 of the treatment application. During the measurement time, air temperature and relative humidity (Extech's RHT510 Hygro-Thermometer Psychrometer, Extech Instruments, Taiwan) were measured to correct gas concentrations during flux calculations.

Lids were half-open after NH_3 measurements to replicate typical storage conditions, to circulate the air and to minimize the moisture loss. At the end of the storage period, the slurry was well mixed with the biochar or LECA to monitor any effects of the mixing process on emissions. Stirring was carried out for 3-min using an electrical stirrer. Subsequently, the containers were closed and NH_3 concentrations measured. Measurements were continued for two occasions (day 107 and 113) after mixing. Loss of moisture from each container was determined at the end of the experiment by subtracting the final weight of the slurry to the initial weight.

2.5. Flux calculations

Daily fluxes of NH_3 (F_{NH3}) were calculated as:

$$F_{NH_3} = \left(\frac{C_{60} - C_0}{t_{60} - t_0}\right)\left(\frac{V\ M}{A\ V_m}\right) \quad (2)$$

Where F_{NH3} is the daily flux of NH_3 (mg N m^{-2} h^{-1}); C_0 and C_{60} are the NH_3 (μL L^{-1}) concentration determined at zero min (t_0; ambient air) and at 60 min (t_{60}) after closure of the containers, respectively, and the time is expressed in hour (h). V is the bucket headspace volume (L); A is the slurry surface area (m^2); M is the molar mass of NH_3 (g mol^{-1}); and V_m is the volume of 1 mol of gas (L mol^{-1}) which was calculated using standard atmospheric pressure and temperature measured at the time of gas sampling.

Cumulative emission was calculated by linear interpolation of observed NH_3 fluxes at two adjacent dates. Emissions factor (EF) was calculated as a net loss of NH_3–N to total ammoniacal N (TAN) and total N (TN) present in the bucket slurry.

Emission reduction efficiency (RE) was calculated as:

$$RE\ (\%) = [(E_{treatment} - E_{control})/E_{control}]x\ 100 \quad (3)$$

Where $E_{treatment}$ and $E_{control}$ are the cumulative emissions from treatment added and control slurry.

2.6. Statistical analysis

The data were analysed using the *anova* function after fitting the data into the '*lme*' model of the '*nlme*' package using the restricted maximum likelihood (REML) method (R-software version 4.1.2). Prior to analysis, the model assumptions, i.e., normal distribution and homogeneity of

Table 3
Cumulative NH_3 emissions and emission factors (EFs) during the experimental period. Emission factors (EFs) were calculated as net loss of ammoniacal N (EF_TAN) and total N (EF_TN) present in the containers in form of NH_3–N. Mean ± standard errors were derived from replicates (n = 3). Significant differences at $p < 0.05$ are represented by different letters.

	Cumulative NH_3–N ($g\ m^{-2}$)	EF_TAN (%)	EF_TN (%)
Miscanthus (MB)	17.0 ± 1.1 ab	39.3 ± 2.6 ab	21.9 ± 1.4 ab
Activated Miscanthus (AMB)	13.3 ± 1.8 c	30.5 ± 4.2 c	17.0 ± 2.3 c
Digestate (DB)	15.3 ± 0.7 abc	35.3 ± 1.7 abc	19.7 ± 1.0 abc
Activated digestate (ADB)	12.8 ± 1.0 c	29.4 ± 2.2 c	16.4 ± 1.2 c
LECA	14.1 ± 0.4 bc	32.5 ± 0.9 bc	18.1 ± 0.5 bc
Control (Ctrl)	17.8 ± 0.8 a	41.0 ± 1.9 a	22.9 ± 1.1 a

Table 4
Mineral N content in the floating-biochars at the end of the experiment. Mean ± standard error was derived from replicates n = 2 for all treatment except LECA (n = 3) as the biochar had sunk in several cases.

Treatments	NH_4 ($mg\ N\ kg^{-1}$)	NO_3 ($mg\ N\ kg^{-1}$)
Miscanthus (MB)	490 ± 189 a	1.8 ± 0.4 a
Activated miscanthus (AMB)	621 ± 4 a	1.8 ± 0.0 a
Digestate (DB)	369 ± 261 a	1.4 ± 1.0 a
Activated digestate (ADB)	712 ± 263 a	1.6 ± 1.3 a
LECA	1393 ± 804 a	2.6 ± 1.5 a

Table 5
Properties of biochars used in the experiment.

	Density ($g\ cm^{-3}$)	pH
Miscanthus (MB)	0.44	10.4
Activated Miscanthus (AMB)	0.49	4.8
Digestate (DB)	0.69	11.0
Activated digestate (ADB)	0.70	8.9
LECA	0.25	–

variance, were tested using diagnostic plots. Mean differences between treatments were performed via pairwise comparisons using the adjusted Tukey method available in the function *emmeans*. The threshold for hypothesis rejection was $p < 0.05$.

3. Results and discussions

3.1. Slurry properties

Properties of the slurry prior to and after the experiment were compared (Table 1). Moisture loss from the different treatments was consistent during the experiment period (data not shown). The DM of the slurry was similar prior to and after the experiment compared to the unamended slurry. The DM had increased in the biochar amended treatments while TN and pH were significantly reduced during the experimental period, most likely due to the loss of N as NH_3 because the conversion of NH_4^+ to NH_3 is an acid producing reaction. TAN reduced significantly during experimental period in the treatment without cover on top (Ctrl), but showed no difference in the treatments with bio-covers (Table 1). Ash content was increased in the Ctrl, DB and ADB treatment after the experiment.

Physico-chemical properties of the biochars are presented in Table 2. The Brunauer–Emmett–Teller (BET) surface area, phosphorus, ash content and conductivity of miscanthus biochar were lower than digestate biochar. In turn, total C, potassium, calorific value and silicon content were higher in the miscanthus biochar than the digestate biochar. The NH_3 reduction efficiency may increase with a higher surface area (Covali et al., 2021) or ash content (Yu et al., 2016) due to NH_3 adsorption capacity. This is partially agreed as the NH_3 emissions reduction efficiency was higher for the digestate biochar than the miscanthus biochar. In fact, the BET, pore structure and micromorphology are related to the carbon in the biochars, and may not have direct relationship to NH_3 absorption efficiency (Yu et al., 2016).

3.2. NH_3 emissions

Ammonia emissions were highly variable during the measurement period within and among the treatments. Significantly lower emissions were observed from activated biochars for a month. After a month, the emissions returned to the same level as the other treatments. The emissions were reduced significantly immediately after stirring of the slurry due to the release of accumulated NH_3 during stirring. The emissions were highly variable in the subsequent measurements.

In this experiment, application of non-activated biochar on the slurry surface did not decrease NH_3 emissions compared to the Ctrl as reported in the previous studies (Hung et al., 2022; Maurer et al., 2017; McGuiggan et al., 2022). This is however in contrast to the other studies where NH_3 emissions were significantly reduced with the application of biochar (Table S1). The reduction in emissions with a bio-cover is related to the resistance to transfer of NH_3 from the slurry surface to the atmosphere (Holly and Larson, 2017; Sommer, 1997). This resistance increases with an increase in the thickness of the covering materials. The ineffectiveness of non-activated biochars to reduce the emissions in this study may be related to the shallow depth (7 mm) of biochar.

Lower cumulative NH_3 emissions from the activated biochars compared to the Ctrl show that activated biochar is an effective bio-cover for NH_3 emission mitigation (Table 3). Similar to this study, previous studies also found lower emissions using activated biochar as a slurry cover (Covali et al., 2021; Häni et al., 2012). Activation of biochar increases the surface area and porosity and also creates new functional groups which increase NH_3 adsorption (Sajjadi et al., 2019; Tsang et al., 2007). Comparing mean adsorption of NH_4^+-N among biochars, we found a higher adsorption in the activated biochar than in the non-activated biochar. Despite this, they were not statistically different due to higher variability (Table 4). Similarly, the pH of the miscanthus biochar dropped from 10.4 to 4.8 with activation by H_3PO_4 (Table 5). However, the pH of digestate biochar was still 8.9 after activation. With application of AMB, slurry surface pH might lower and thus lower NH_3 emission. This may explain why there were lower emissions from AMB for a month compared to ADB (Fig. 1). Subsequently, the reduction potential quickly dropped, indicating that the slurry surface pH and the pH of AMB increased due to the buffering capacity of the slurry. Overall, it is hypothesised that the NH_3 emission is reduced by the combined effects of an increase in the porosity, surface area and functional groups of biochar and a decrease in the slurry surface pH.

The emission mitigation potential of activated biochars was reduced as the storage period progresses (Table 6). AMB and ADB reduced the emission by 51% and 37%, respectively, during a month of storage. However, the emission mitigation efficiency was reduced respectively to 25% and 28% in AMB and ABD in four months storage period. Previous

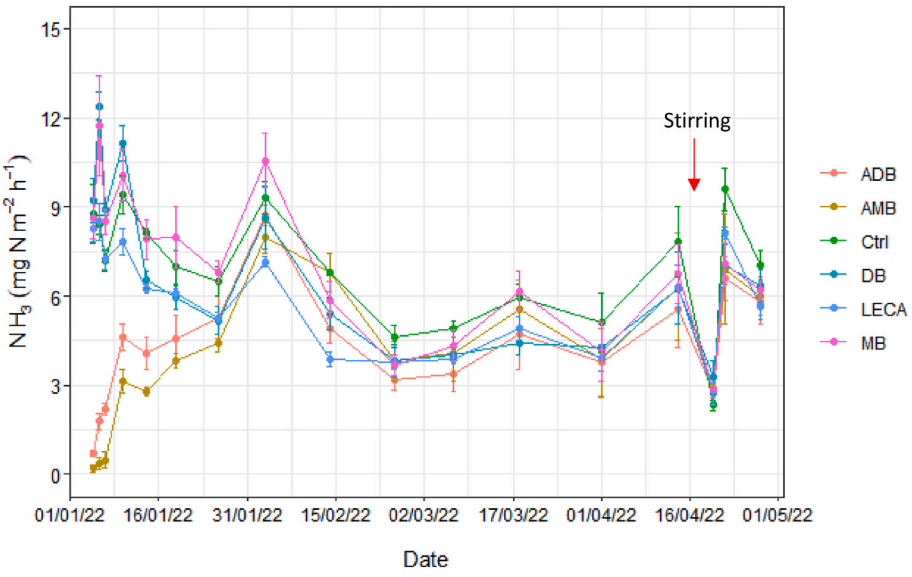

Fig. 1. Temporal dynamics of NH_3 emissions during the experimental period. The data points represent mean values and error bars represent two sided standard errors. Ctrl, control (reference slurry); MB, miscanthus biochar; AMB, activated miscanthus biochar; DB; biochar from solid fraction of digestate; ADB, activated digestate biochar; LECA, lightweight expanded clay aggregate.

Table 6
NH_3 emissions reduction efficiency (RE %) of different floating-covers used in the experiment in comparison to the reference slurry. Negative values represent higher emissions from the floating-cover treatments than the reference slurry.

	30 days	40 days	61 days	113 days
Miscanthus (MB)	−9	−7	−1	4
Activated Miscanthus (AMB)	51	39	32	25
Digestate (DB)	5	7	10	14
Activated digestate (ADB)	37	31	31	28
LECA	16	21	22	21

studies also observed similar trends (Maurer et al., 2017; Meiirkhanuly et al., 2020), indicating that periodic application of biochar might further improve emission reduction potential (Chen et al., 2021).

The LECA layer thickness used in this experiment was lower than used in the previous research in order to make the experiment more comparable to the selected biochar layer thickness. LECA reduced NH_3 emissions by 21% during the experimental period. Misselbrook et al. (2016) found a 61% reduction in NH_3 with 7 cm LECA layer on top. Balsari et al. (2006) observed a 73% reduction in the emission with a 10 cm layer. Our study, along with the previous research, suggest that LECA can be used as a floating cover to reduce NH_3 emission from the slurry store and it is likely that the effectiveness would increase with increasing the depth of LECA layer on the slurry surface.

3.3. Emission factors

Losses of NH_3 as a percentage of TAN (EF _TAN) and TN (EF_TN) ranged from 29.4-41.0% and 17.0–22.9%, respectively (Table 3). In Ctrl, 41.0% of TAN was emitted as NH_3–N, which is slightly higher than average emissions factors (19 ± 12%) calculated from some European studies (Sommer et al., 2019), but similar to the pilot scale study in the UK where they found 40.6% of TAN emitted as NH_3 (Misselbrook et al., 2005). In comparison to Ctrl, NH_3–N loss was significantly lower in ADB, AMB and LECA treatments, but emissions were not different from MB and DB treatments.

4. Conclusions

This study demonstrated that activated biochars and LECA are potential floating-covers for the reduction of NH_3 emissions during slurry storage. In practice, such covers would be more applicable to outdoor stores, which do not undergo surface disruption until mixing, rather than under slat stores, which would have a constant addition of animal slurry from the slatted floors above, disrupting a potential bio-cover. The emissions reduction efficiency of such a bio-cover decreased as storage time progressed. For example, the emission reduction efficiency of activated biochars was 37–25% in the first month and reached 25–28% in the realistic storage period of four months. The effectiveness of LECA to reduce NH_3 emissions was promising even at a shallow bio-cover depth. The effectiveness may increase further by increasing the cover depth. Non-activated biochar of digestate and miscanthus may not be an effective bio-cover to reduce emissions at the current applied depth of 7 mm. However, the effectiveness may increase with thicker applications, but this may create financial burden and manageability problems during slurry stirring, pumping and field application. Similarly, impact of the floating covers to reduce NH_3 emissions, soil N and C cycling and microbiomes after field application need to be assessed in the future research.

Author Statement

Khagendra Raj Baral: Conceptualization, Methodology, Resources, Investigation, Formal analysis, Data curation, Writing – original draft, Review & editing. **John McIlroy:** Conceptualization, Methodology, Review & editing. **Gary Lyons:** Conceptualization, Methodology, Resources, Review & editing. **Chris Johnston:** Conceptualization, Methodology, Review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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References

Ahmedna, M., Johns, M., Clarke, S., Marshall, W., Rao, R., 1997. Potential of agricultural by-product-based activated carbons for use in raw sugar decolourisation. J. Sci. Food Agric. 75, 117–124. https://doi.org/10.1002/(SICI)1097-0010 (199709)75:1<117::AID-JSFA850>3.0.CO;2-M.

Antonangelo, J.A., Sun, X., Zhang, H., 2021. The roles of co-composted biochar (COMBI) in improving soil quality, crop productivity, and toxic metal amelioration. J. Environ. Manag. 277, 111443 https://doi.org/10.1016/j.jenvman.2020.111443.

Balsari, P., Dinuccio, E., Gioelli, F., 2006. A low cost solution for ammonia emission abatement from slurry storage. Int. Congr. 1293, 323–326. https://doi.org/10.1016/j.ics.2006.02.045.

Chen, B., Koziel, J.A., Banik, C., Ma, H., Lee, M., O'Brien, S.C., Li, P., Andersen, D.S., Białowiec, A., Brown, R.C., 2021. Mitigation of gaseous emissions from stored swine manure with biochar: effect of dose and reapplication on a pilot-scale. Atmosphere 12, 96. https://doi.org/10.3390/atmos12010096.

Covali, P., Raave, H., Escuer-Gatius, J., Kaasik, A., Tõnutare, T., Astover, A., 2021. The effect of untreated and acidified biochar on NH3-N Emissions from slurry digestate. Sustainability 13, 837. https://doi.org/10.3390/su13020837.

DAERA, 2022. Northern Ireland environmental statistics report 2020. Department of agriculture , enviroment and rural affairs (DAERA). Available at: https://www.daera-ni.gov.uk/publications/northern-ireland-environmental-statistics-report-2020.

de Vries, W., 2021. Impacts of nitrogen emissions on ecosystems and human health: a mini review. Current Opinion in Environmental Science & Health 21, 100249. https://doi.org/10.1016/j.coesh.2021.100249.

Dougherty, B., Gray, M., Johnson, M.G., Kleber, M., 2017. Can biochar covers reduce emissions from manure lagoons while capturing nutrients? J. Environ. Qual. 46, 659–666. http://10.2134/jeq2016.12.0478.

FAO, 2022. Animal production and health. Food Agriculture Organization of the United Nation. Available at: https://www.fao.org/ag/againfo/home/en/index.htm.

Feng, D., Guo, D., Zhang, Y., Sun, S., Zhao, Y., Chang, G., Guo, Q., Qin, Y., 2021. Adsorption-enrichment characterization of CO2 and dynamic retention of free NH3 in functionalized biochar with H2O/NH3·H2O activation for promotion of new ammonia-based carbon capture. Chem. Eng. J. 409, 128193 https://doi.org/10.1016/j.cej.2020.128193.

Häni, C., Kupper, T., Jocher, M., Neftel, A., Sintermann, J., 2012. Amendment of Biochar to Slurry: a Possibility to Mitigate Ammonia Emissions, vol. 126. Emissionsof Gasand Dust from Livestock.

Holly, M.A., Larson, R.A., 2017. Thermochemical conversion of biomass storage covers to reduce ammonia emissions from dairy manure. Water, Air, Soil Pollut. 228, 1–12. https://doi.org/10.1007/s11270-017-3588-x.

Hung, C.-Y., Hussain, N., Husk, R., Whalen J, B.K., AnneNaeth, M., 2022. Ammonia volatilization from manure mixed with biochar. Can. J. Soil Sci. 102, 177–186. https://doi.org/10.1139/cjss-2021-0029.

Kavanagh, I., Burchill, W., Healy, M.G., Fenton, O., Krol, D.J., Lanigan, G.J., 2019. Mitigation of ammonia and greenhouse gas emissions from stored cattle slurry using acidifiers and chemical amendments. J. Clean. Prod. 237, 117822 https://doi.org/10.1016/j.jclepro.2019.117822.

Liu, M., Liu, C., Liao, W., Xie, J., Zhang, X., Gao, Z., 2021. Impact of biochar application on gas emissions from liquid pig manure storage. Sci. Total Environ. 771, 145454 https://doi.org/10.1016/j.scitotenv.2021.145454.

Maurer, D.L., Koziel, J.A., Kalus, K., Andersen, D.S., Opalinski, S., 2017. Pilot-scale testing of non-activated biochar for swine manure treatment and mitigation of ammonia, hydrogen sulfide, odorous volatile organic compounds (VOCs), and greenhouse gas emissions. Sustainability 9, 929. https://doi.org/10.3390/su9060929.

McGuiggan, H., Olave, R., Reid, N., 2022. Biochar addition to stored slurry reduces carbon dioxide, nitrous oxide, and hydrogen sulphide, but not ammonia, methane, or total greenhouse gas emissions. https://doi.org/10.2139/ssrn.4076702.

Meiirkhanuly, Z., Koziel, J.A., Chen, B., Białowiec, A., Lee, M., Wi, J., Banik, C., Brown, R.C., Bakshi, S., 2020. Mitigation of gaseous emissions from swine manure with the surficial application of biochars. Atmosphere 11, 1179. https://doi.org/10.3390/atmos11111179.

Misselbrook, T., Hunt, J., Perazzolo, F., Provolo, G., 2016. Greenhouse gas and ammonia emissions from slurry storage: impacts of temperature and potential mitigation through covering (pig slurry) or acidification (cattle slurry). J. Environ. Qual. 45, 1520–1530. https://doi.org/10.2134/jeq2015.12.0618.

Misselbrook, T.H., Brookman, S.K., Smith, K.A., Cumby, T., Williams, A.G., McCrory, D. F., 2005. Crusting of stored dairy slurry to abate ammonia emissions: pilot-scale studies. J. Environ. Qual. 34, 411–419. https://doi.org/10.2134/jeq2005.0411dup.

Nartey, O.D., Liu, D., Uwamungu, J.Y., Luo, J., Lindsey, S., Di, H.J., Chen, Z., Yuan, J., Ding, W., 2021. Corn cobs efficiently reduced ammonia volatilization and improved nutrient value of stored dairy effluents. Sci. Total Environ. 769, 144712 https://doi.org/10.1016/j.scitotenv.2020.144712.

Pereira, J.L.S., Figueiredo, V., Pinto, A.F.M.A., Silva, M.E.F., Brás, I., Perdigão, A., Wessel, D.F., 2020. Effects of biochar and clinoptilolite on composition and gaseous emissions during the storage of separated liquid fraction of pig slurry. Appl. Sci. 10, 5652. https://doi.org/10.3390/app10165652.

Petersen, S.O., Hutchings, N.J., Hafner, S.D., Sommer, S.G., Hjorth, M., Jonassen, K.E.N., 2016. Ammonia abatement by slurry acidification: a pilot-scale study of three finishing pig production periods. Agric. Ecosyst. Environ. 216, 258–268. https://doi.org/10.1016/j.agee.2015.09.042.

Sajjadi, B., Zubatiuk, T., Leszczynska, D., Leszczynski, J., Chen, W.Y., 2019. Chemical activation of biochar for energy and environmental applications: a comprehensive review. Rev. Chem. Eng. 35, 777–815. https://doi.org/10.1515/revce-2018-0003.

Singh, B., Dolk, M.M., Shen, Q., Camps-Arbestain, M., 2017. Biochar pH, electrical conductivity and liming potential. Biochar: A guide to analytical methods 23.

Sommer, S.G., 1997. Ammonia volatilization from farm tanks containing anaerobically digested animal slurry. Atmos. Environ. 31, 863–868. https://doi.org/10.1016/S1352-2310(96)00250-6.

Sommer, S.G., Webb, J., Hutchings, N.D., 2019. New emission factors for calculation of ammonia volatilization from European livestock manure management systems. Front. Sustain. Food Syst. 3. http://10.3389/fsufs.2019.00101.

Sun, X., Cheng, P., Wang, H., Xu, H., Dang, L., Liu, Z., Lei, Z., 2015. Activation of graphene aerogel with phosphoric acid for enhanced electrocapacitive performance. Carbon 92, 1–10. https://doi.org/10.1016/j.carbon.2015.02.052.

Trinh, T.K., Tsubota, T., Takahashi, S., Mai, N.T., Nguyen, M.N., Nguyen, N.H., 2020. Carbonization and H3PO4 activation of fern Dicranopteris linearis and electrochemical properties for electric double layer capacitor electrode. Sci. Rep. 10, 1–10. https://doi.org/10.1038/s41598-020-77099-7.

Tsang, D.C.W., Hu, J., Liu, M.Y., Zhang, W., Lai, K.C.K., Lo, I.M.C., 2007. Activated carbon produced from waste wood pallets: adsorption of three classes of dyes. Water Air Soil Pollut. 184, 141–155. http://10.1007/s11270-007-9404-2.

Wang, B., Lehmann, J., Hanley, K., Hestrin, R., Enders, A., 2016. Ammonium retention by oxidized biochars produced at different pyrolysis temperatures and residence times. RSC Adv. 6, 41907–41913. https://doi.org/10.1039/C6RA06419A.

Xu, H., Cai, A., Wu, D., Liang, G., Xiao, J., Xu, M., Colinet, G., Zhang, W., 2021. Effects of biochar application on crop productivity, soil carbon sequestration, and global warming potential controlled by biochar C: N ratio and soil pH: a global meta-analysis. Soil Tillage Res. 213, 105125 https://doi.org/10.1016/j.still.2021.105125.

Yu, Q., Xia, D., Li, H., Ke, L., Wang, Y., Wang, H., Zheng, Y., Li, Q., 2016. Effectiveness and mechanisms of ammonium adsorption on biochars derived from biogas residues. RSC Adv. 6, 88373–88381. https://doi.org/10.1039/C6RA16913A.