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^{15}N mass balance technique for measuring ammonia losses from soil surface-applied slurries containing various additives

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Abstract

Background: Anthropogenic ammonia emissions, primarily derived from agriculture, lead to air pollution, soil acidification, and surface water eutrophication, all of which adversely affect human health and ecosystems. Slurry treatment technologies in the form of additives represent an underutilized means of reducing gaseous emissions. Information regarding the potential of additives to reduce ammonia in soil surface-applied slurries is scarce.

Aim: This study aims to develop a ^{15}N mass balance technique to quantitatively measure ammonia losses from different slurries containing multiple additives that are applied to outdoor soil-filled containers.

Methods: The experiments were performed under free-air conditions. Isotopically labeled slurries from biogas, cattle, and pigs containing 18 additives were surface-applied to soil-filled containers and exposed for 72 or 48 h. The additives included inorganic and organic adsorbents, five amounts of sulfuric acids, molasses ± effective microorganisms, and water dilution. After termination of the ammonia loss period, a suite of soil preparation steps for the quantitative recovery of the labeled ammonium remaining in the soil was developed, and subsequently the loss of NH_4-N was determined.

Results: In the control treatments, ammonia losses from biogas, cattle slurries, and pig slurries averaged 54.4%, 33.9%, and 11.0%, respectively. The adsorbents did not decrease or only slightly decreased ammonia emissions. Ammonia abatement by sulfuric acid was nearly complete at pH values of 5.9 and 5.8 for the biogas and pig slurry, respectively, and about 80% at pH 5.2 for the cattle slurry. In comparison, more moderately decreased pH values with sulfuric acid showed a similar reduction as molasses and a 1:1 dilution for the three slurries. Adding microorganisms to the molasses did not further decrease ammonia losses.

Conclusion: The newly developed ^{15}N mass balance technique, which allows a precise estimate of ammonia losses, can serve as a reference method to assess ammonia losses from field-applied slurries containing various additives and as a standard comparison technique for other ammonia measurement techniques.

KEYWORDS
ammonia abatement, ammonia emission, ammonia loss, isotope, manure, slurry

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1 INTRODUCTION

Anthropogenic ammonia (NH_3) emissions, with the agricultural industry contributing about 95% of these emissions (Wyer et al., 2022), have led to air pollution, soil acidification, and surface water eutrophication, resulting in tremendous damage to human health and ecosystems (Giannadaki et al., 2018; Hu & Schmidhalter, 2021; Pozzer et al., 2017). Thus, mitigating NH_3 emissions is of high priority, and legislation in the European Union (EU) has been established to implement mitigation strategies for these emissions.

In the EU, NH_3 emissions are ~80%–90% from livestock and digestates; this suggests that future mitigation measures should focus on reducing NH_3 emissions from the management chains of livestock slurry, manure, and digestates to comply with the NEC 2030 target. NEC Directive 2016/2284/EU sets national reduction targets for NH_3 emissions in individual EU countries.

Slurry treatment technologies using additives represent an underutilized means of reducing gaseous emissions and preserving the nutrient content of stored manure (Thorn et al., 2022). The reduction of NH_3 volatilization is possible, particularly with adsorbents and acidifying additives, and there is potential to develop further practical and cost-effective additives in this area (McCrory & Hobbs, 2001; Ye et al., 2022). The adsorbents can bind the ammonium, thereby reducing ammonia volatilization. Pereira, Perdigão, Marques, et al. (2022) found in a laboratory study that during short-term storage, NH_3 emissions were reduced by 58% as a result of acidification and by 20% as a result of biochar. Previous studies (Kalus et al., 2019) have reported that adding biochar (1%–12%, w/w) to animal manure reduces ammonia emissions by 12%–77%. Notably, biochar made from hardwoods is a better adsorbent than corncobs and mixed sawdust (Kizito et al., 2016). Much lower adsorption by Australian zeolites than by other zeolite sources was reported by Wijesinghe et al. (2016). The acidification of slurry is a treatment known to reduce ammonia emissions and is currently applied at the farm scale in Denmark by adding concentrated sulfuric acid (H_2SO_4). Lim et al. (2017) showed that soluble carbohydrates can mitigate ammonia emissions by acidifying stored manure slurry. Soluble carbohydrates, such as glucose or molasses, are a reasonable choice for animal farmers to replace expensive microbial additives. Effective microorganisms (EMs) can enhance slurry biodegradation. However, Van der Stelt et al. (2007) found that the use of EMs as additives to livestock manure did not significantly reduce ammonia emissions.

Therefore, standard, independent test procedures are required to evaluate the efficacy of additives (McCrory & Hobbs, 2001). Such tests should be simple and should quantify the capacity of the additive to perform as claimed and therefore require further studies in this area. In practice, farmers use many additives, but their effects remain unclear. We selected a range of locally available additives based on suggestions from the Biological Farmers' Association. In this study, chemical and biological additives were used to mitigate ammonia emissions from surface-treated cattle, pigs, and biogas slurries.

In this context, we developed a new ^{15}N-balance method for quantifying ammonia loss from soil-filled containers placed under outdoor conditions. This study investigated the effects of 18 additives including controls, each with three replicates, a total of 162 treatments, on ammonia loss in cattle, pig, and biogas slurries. The new nitrogen mass balance technique showed in pre-experiments, with the experimental soil Steinach, that the recovery of ^{15}N from 48 h incorporated slurry was nearly complete with about ±2% (Schmidhalter, 2018; Schmidhalter et al., 2017). This allows for the quantitative determination of ammonia losses using the technical steps described in this study.

Various techniques, including enclosure or chamber techniques, micrometeorological techniques, and N balance/difference methods, have been used to measure ammonia loss based on their advantages and disadvantages. Some preferences have been given to micrometeorological methods such as the state-of-the-art integrated horizontal flux method, which requires a large field size and is not amenable to numerous treatments. However, no method has been developed to depict absolute ammonia losses. Absolute emissions should be evaluated using non-interference techniques if possible (Harper, 2005). More recent measurements show substantially lower emission factors, which call for a new measurement series to validate the various measurement approaches and derive revised inputs for inclusion in emission inventories (Sintermann et al., 2012).

Therefore, to assess ammonia losses from an increased number of treatments, which involve smaller exposure areas under outdoor conditions, we have worked on developing and evaluating a modified ^{15}N-balance technique that might serve as a potential reference technique, fulfilling the requirements of technical simplicity, cheapness, precision, and applicability to small-plot experimentation to evaluate multiple and replicated treatments and be amenable to use on various sites. We expect that this novel method will allow the quantitative assessment of ammonia losses.

We further expect a different mitigation potential of additives, with acidifying additives being more effective than adsorbents, and in line with the previous experience of good slurry dilution effects. Because the ammonia losses among the different slurries most likely vary, the effects of the additives may also vary owing to the different slurry properties.

2 MATERIALS AND METHODS

2.1 Experimental site

The experiments were performed under free air conditions outside the Research station Dürnast in south-east Germany near Freising using soil-filled plastic containers, 11.8 cm in diameter and 10 cm in height with a volume of 1093 cm^3. Steinach showed sizeable ammonia losses from banded slurries in previous experiments. The properties of the Steinach soil were 11% sand, 79% silt, 10% clay, pH 6.3, OH^- buffer capacity 5.03, cation exchange capacity (CEC) 14.73 meq/100 g soil, and 0.370 at.%^{15}N. The soil pH was measured in a 1:2.5 soil/0.01 M $CaCl_2$ suspension. Soil texture was determined using the pipette method (Gee & Bauder, 1986), soil pH buffer capacity was determined according to Kissel et al. (2012), and the CEC was deter-

TABLE 1 Experimental schedule and exposure time.

Date	Number of Experiment	Additives	Exposure time (hour)
29.03.2019	Experiment 1	5 adsorbents + control	72
16.04.2019	Experiment 2	5 amounts of 5 M sulfuric acid + control	48
24.04.2019	Experiment 3	Molasses ± effective microorganisms (EM) + control; dilution by water (100%, 50%) + control	48

mined according to Mehlich (1948) and modified by Meiwes et al. (1984).

The experimental soil was dried and sieved to 5 mm; any coarse debris (stones and roots) was removed before sieving. Subsequently, the soil was crushed and homogenized in an SR 300 rotor beater mill (Retsch), and then, by intensive further mixing in a concrete mixer, brought to 25% water-holding capacity. Before use, the soil was stored in 25 kg covered containers. Shortly before use, the soil was mixed again, and the plastic containers were filled with ~1000 g of moist soil. The exact weight of the soil-filled containers, including the tare, was gravimetrically assessed, and the dry weight of the soil was determined as well. All the soils were then stored in containers covered with a lid and kept in a refrigerator until the slurry was applied.

2.2 | Experimental slurries

Three different slurries, namely cattle, pig, and biogas, were used, which had the following properties: cattle slurry: NH_4-N 0.198%, N_t 0.37, dry matter 7.67%, pH 7.2; pig slurry: NH_4-N 0.284%, N_t 0.35, dry matter 5.31%, pH 7.7; and biogas slurry: NH_4-N 0.343%, N_t 0.58, dry matter 9.16%, pH 7.9. Total N and NH_4-N were determined in fresh slurry subsamples using the Kjeldahl technique (Vapodest 12; C. Gerhardt GmbH & Co., KG) both before and after digestion with concentrated H_2SO_4.

Before application, all the slurries were passed through a 5-mm sieve of mesh and stirred for 2 min in the storage container. Following this, 3 L of each slurry was homogenized for 5 min using a standing mixer. Only the pig slurry exhibited some sedimentation and was continuously stirred using a magnetic stirrer for further applications.

2.3 | Isotopic labeling of the experimental slurries and addition of additives

Ammonium sulfate with 95% ^{15}N was used to label the slurries. All the slurries were enriched to 4.00 at.%^{15}N and thoroughly mixed. Until used, the labeled slurries were sealed in an airtight container and stored in a refrigerator at 8°C.

Because of the large number of additives (each with three replicates, a total of 162, which are subsequently described), the experiment was split into three sections conducted at three different times because the application time would last too long, leading to possible differences in ammonia emissions (Table 1).

All commercially available additives were added according to the suppliers' information. Due to labor shortages, the first experiment lasted 24 h longer than the other two. However, based on more detailed temporal pre-experiments, we do not expect an effect because most of the ammonia is lost shortly after application under the chosen meteorological conditions.

The first group of additives included five adsorbents (Experiment 1): leonardite (0–4 mm, sieved), charcoal (ground), bentonite (ground), dolomite (ground liquid), and Hersbrucker rock powder (ground). After the addition of the slurries, they were shaken for 24 h before application to the soil surface.

The second group contained five amounts of sulfuric acid, two dilutions of water (100%, 50%), and a control for each (Experiment 2), which were added shortly before application.

The third group of additives included sugar beet molasses and sugar beet molasses with effective microorganisms (homofermentative lactic acid bacteria in liquid form) (Experiment 3). This group of additives required a longer pre-incubation time (see below) until the pH ceased to decrease.

The additives are briefly described and characterized below. Where no further information from commercial products was available, more general information characterizing the additives has been provided.

2.4 | Experiment 1: Adsorbents

Leonardite (Lösl) is derived from the oxidation of lignite. The mineral is black-brown, soft, transparent, and shiny. It is rich in humic acids; ammonium can be adsorbed onto humic substances. It also contains additional fulvic acids. The CEC is very high and weighs 750 kg m^{-3}; the inner surface is high with 5 m^2 g^{-1} and weighs 750 kg m^{-3}. Leonardite was characterized by 0.789% N and 0.367 at.%^{15}N.

Charcoal (Fetzer Rohstoffe and Recycling GmbH) is enriched in carbon by heating while preventing oxygen access. The carbon content is 80%, and the CEC is 500 mol kg^{-1}. The experimental charcoal had 0.256% N and 0.366 at.%^{15}N.

Bentonite (Franz Donderer) is a rock powder derived from sediment. The main clay mineral is montmorillonite, which also contains quartz, calcite, pyrite, illite, biotite, and feldspar. Bentonite was characterized by 0.013% N and 0.370 at.%^{15}N.

TABLE 2 Amounts of adsorbents added to the slurries.

Additive	Amount added kg m^{-3}
Leonardite	30.00
Charcoal	2.50
Bentonite	30.00
Dolomin	50.00
Hersbrucker rock powder	50.00

Dolomin (DÜKa Düngegesellschaft mbH) is a liquid carbonate fertilizer dissolved in water and derived from calcium carbonate, dolomite, and dendritic sedimentary rocks. Ninety percent of the fertilizer is finer than 0.02 mm, consisting of 27% $CaCO_3$, 4% $MgCO_3$ (Düka, 2019), 16% alkaline ingredients, clay minerals, and silicic acid. Dolomin was characterized by 0.022% N and 0.370 at%^{15}N.

Hersbrucker rock powder (DÜKa Düngegesellschaft mbH) from the Jurassic formation consists of 28%–32% illite, vermiculite, and interstratified clays. Ninety percent of the powder is finer than 0.09 mm. The Hersbrucker rock powder consists of 20%–22% calcium oxide, 6%–7% magnesium oxide, 2%–3% potassium oxide, 3%–4% iron, 6%–7% aluminum, and 24%–28% silicic acid (Düka, 2019). The rock powder was characterized by 0.004% N and 0.393 at.%^{15}N.

The amount added in the kg m^{-3} slurry is indicated in Table 2. After addition, the slurries were shaken for 24 h to obtain a homogeneous distribution.

2.5 | Experiment 2: Acidifying by sulfuric acid and dilution by water

The second group included six concentrations of 5 M sulfuric acid, including the control, two dilutions in water (100%, 50%), and the control without dilution. Sulfuric acid delivers 10.6 kg S when applied with 18.6 m^3 slurry per hectare, the intended application amount. Known amounts of sulfuric acid were added based on pre-experiments the day before the slurry was applied to the containers using a pipette and a magnetic stirrer. A pH meter was used to determine the final pH shortly before application. The final pH values deviated slightly from the intended values and are indicated in Table 3.

As for the dilution of the slurries, 50% and 100% were chosen and compared with a non-diluted slurry (control), which was prepared shortly before the slurry was applied to the soil surface.

2.6 | Experiment 3: Sugar beet molasses ± effective microorganisms

The third group of additives included sugar beet molasses and effective microorganisms (homofermentative lactic acid bacteria; Table 4). These compounds required a longer reaction time before use and were allowed to react for 7 days until no further pH decrease was noticed based on pre-experiments. Warm water was used to add the molasses.

TABLE 3 Amount (L m^{-3}) of 5 M sulfuric acid added to the slurries, target pH value, and final pH value after acidification.

Slurry type	Addition (L m^{-3})	Target pH value	Final pH value
Cattle slurry	0	7.2	7.2
	1	7	7.1
	4.2	6.5	6.6
	11.3	6	6.2
	15.7	5.5	5.7
	23.3	5	5.2
Pig slurry	0	7.7	7.7
	4	7	7.0
	10.7	6.5	6.5
	16.7	6	6.1
	20.7	5.5	5.8
	25.3	5	5.2
Biogas slurry	0	7.9	7.9
	8.7	7	7.1
	27.3	6.5	6.7
	34.7	6	6.3
	38	5.5	5.9
	41.3	5	5.6

Note: Concentrated sulfuric acid (96%) has a molarity of 17.966 mol L^{-1}.

TABLE 4 Carbohydrate/microbiological (effective microorganism [EM]) additives.

Additives	Application rate
Sugar beet molasses	50 kg m^{-3}
Sugar beet molasses + EM	50 kg m^{-3} + 50 kg m^{-3}

Sugar beet molasses was obtained from Meika Tierernährung GmbH. Carbohydrates may decrease through degradation at a pH below 6.0. The sugar beet molasses had a dry weight content of 770 g kg^{-1} and a sugar content of 629 g kg^{-1} dry weight carbohydrates.

Homofermentative lactic acid bacteria were obtained from Dr. Pieper Technology and Product Development GmbH. Microbial acidification may occur through the addition of easily degradable carbohydrates.

2.7 | Slurry application

The targeted amount of slurry was 18.6 m^3 per hectare, corresponding to 20 mL of slurry per 107.5 cm^2 (11.8 cm diameter) of the soil container. The mixed slurries and additives were kept in 100-mL poly flasks for the final application. Before application, the slurries were stirred using a magnetic device, and the pig slurry was stirred during the application as well. A 20-mL aliquot of the slurry was then applied by a 25-mL pipette using an automatic pipette aid in a concentric circle with

FIGURE 1 The experimental setup consists of soil-filled plastic containers placed in couplers surrounded by the experimental soil. The figure further shows the three slurries applied as well as the controls without a slurry.

a slowly rotating plate on which the soil-filled containers were placed. Although the pig slurry could be concentrically applied, the biogas and cattle slurry formed discs (Figure 1). The tip of the pipette was cut back to facilitate the application of the slurry, thus creating a larger opening. All the containers were weighed again before and after receiving the slurry to determine the amount pipetted onto the soil surface.

The application time for the individual slurries containing the adsorbents required 1 h and was started at 07:30 AM in a cool room at the experimental station. Three technicians minimized the application time, with each applying one slurry type. After application, the containers were covered with a lid, which was removed when they were placed outdoors.

2.8 | Outdoor placement of soil-filled containers

To expose the soil-filled plastic containers to outdoor conditions, they were placed in 12 DIN 125 KG sliding couplers, already positioned in a larger plastic container (60 × 40 × 10 cm), holding 12 of these devices surrounded by Steinach soil (Figure 1). Five plastic containers were used in the first experiment. The soil-filled plastic containers were comparably high as the surrounding couplers, allowing undisturbed ambient environmental conditions regarding soil, air temperature, and solar radiation. All the experiments included three replicates of unlabeled slurries. All the treatments were randomized.

2.9 | Termination of ammonia loss period

The ammonia emission in the experiments was terminated by spraying the surface with 12% acetic acid after 72 h or 48 h. Subsequently, the contents of each container were poured and well mixed on aluminum trays, and again, sprayed with 12% acetic acid and air-dried until no further water loss was detected.

2.10 | Soil preparation for ^{15}N-analysis

The next step in coarse grinding and homogenization of the soil from each experimental treatment was to crush it in a percussion rotor mill (Retsch). After each sample was ground, the mill was cleaned with compressed air and ethanol. Before further crushing, which is required for isotope mass spectrometry, each sample was randomized with a sample splitter (Beckel Prüfstoffgeräte), and an aliquot was used for treatment in a vibrating disk mill (Retsch) running at 700 rpm for 2 min, similar to how the device was cleaned after each new sample. The finely crushed soil was kept in small plastic beakers, dried at 60°C for 24 h, weighed in tin capsules, and then analyzed using an isotopic ratio mass spectrometer by Dumas combustion. Based on the weight, the recovery of labeled ammonium was determined, and subsequently the loss of $\mathrm{NH_4}$-N. $\mathrm{NH_4^+}$ recovery was calculated according to the method described by Hauck and Bremner (1976):

$$\mathrm{NH4+-N\%} = 100 \times \frac{\mathrm{n\,Nsample} \times (\mathrm{at.\%\ 15Nsample} - \mathrm{at.\%\ 15Nn.\,r.\,soil})}{\mathrm{n\,NH4+-Nslurry} \times (\mathrm{at.\%\ 15NNH4+-Nslurry} - \mathrm{at.\%\ 15Nn.\,r.\,soil})}, \tag{1}$$

$\mathrm{NH4+-N\%}$ is the recovery of $\mathrm{NH_4^+}$-N" in%, n Nsample is the total milliequivalents of nitrogen found in the sample, at.% 15Nsample is the atom% ^{15}N in the sample, at.% 15Nn. r. soil is the atom% ^{15}N in the soil

TABLE 5 Meteorological parameters during the experiments.

Date	Average daily temperature (°C)	Max (°C)	Min (°C)	Wind speed (m s^{-1})	Rainfall (mm m^{-2})
29.03.2019	8.4	15.2	1.7	0.32	0
30.03.2019	8.1	18.9	−1.04	0.03	0
31.03.2019	9.99	19.82	−0.7	0.08	0
16.04.2019	10.21	19.39	0.52	0.1	0
17.04.2019	11.24	19.46	3.41	0.21	0
24.04.2019	17.07	27.51	4.5	0.59	0
25.04.2019	16.12	26.33	3.7	0.49	0

Abbreviations: Max, maximum; Min, minimum.

not receiving the tracer nitrogen, n NH4 + −Nslurry is the milliequivalent of NH_4^+ in slurry, and at.% 15NNH4 + −Nslurry is the atom% ^{15}N of NH_4^+ in slurry.

2.11 | Meteorological parameters

Meteorological parameters were recorded in the area directly adjoining the experimental site and included average, maximum, and minimum temperatures; wind speed at a height of 2 m; and rainfall (Table 5).

2.12 | Statistical analysis

To determine whether significant differences resulted from adding individual additives to the respective test slurries, a single-factor analysis of variance was carried out to compare the respective additives with the original slurry without additives, followed by a least significant difference *t*-test. Values were derived from the *p*-test with a significance level of $p \leq 0.05$. The values of the losses of NH_4-N from the respective slurries were compared with those of the control treatment without additives.

3 | RESULTS

Ammonia loss from the control treatments receiving no additives from the biogas slurry ranged from 52.7% to 56.4% and averaged 54.4%, from the cattle slurry ranged from 31.9% to 36.1% and averaged 33.9%, and from the pig slurry ranged from 10.2% to 13.4% and averaged 11.0% (Figure 2). The control treatments are denominated in Figure 2 as Control A for the adsorbents, Control M for the molasses, Control pH Original for sulfuric acid, and Control D for the dilution treatment. The slight, however, non-significant differences observed for the control treatments indicated that the ambient conditions exerted no differences. Overall, the results show that biogas lost substantially more ammonia than the cattle slurry and even more than the pig slurry.

In general, we observed that the adsorbent additives hardly influenced the ammonia losses. If differences were observed, positive or negative, they were small; for example, leonardite, charcoal, and dolomin significantly reduced the ammonia losses by 3%, 1%, and 3%, respectively, of the biogas slurry, whereas bentonite and rock powder significantly increased ($p \leq 0.01$) the ammonia losses by 2% and 3% of the cattle slurry. No differences were observed in the pig slurry.

For all three slurry types, molasses and molasses with effective microorganisms significantly decreased ammonia losses compared to the control treatment. No difference was observed between the molasses and molasses treatments with effective microorganisms. Ammonia losses were reduced by molasses and molasses with effective microorganisms by 43% and 40% for the biogas slurry, 44% and 50% for the cattle slurry, and 34% and 5% for the pig slurry (Figure 3). Overall, the relatively low emission levels of the pig slurry caused only moderate absolute reductions but increased relative losses.

Sulfuric acid decreased the ammonia losses most substantially for all the slurries based on the pH values; for example, ammonia abatement by sulfuric acid was nearly complete at pH values of 5.9 and 5.8 for the biogas and pig slurry and about 80% at pH 5.2 for the cattle; slurry ammonia losses were reduced by 69% at pH 6.7 for the biogas slurry, by 53% at pH 6.2 for the cattle slurry, and by 48% at pH 6.5 for the pig slurry (Figure 3). However, one should consider that the required amounts of 5 M H_2SO_4 amounted to 27.3 L, 11.3 L, and 10.7 L for the biogas, cattle, and pig slurries, respectively. When expressed as concentrated sulfuric acid, these amounts translate to 7.6 L, 3.1 L, and 3 L. Except for the pH values of 7.1 and 7.0 for the cattle and pig slurries, respectively, all the losses at the decreased pH values were significant ($p \leq 0.01$).

The 1:1 water dilution substantially reduced the ammonia losses by 39%, 50%, and 58% for the biogas, cattle, and pig slurries, respectively (Figure 3). The 1:0.5 water dilution was less efficient and was not statistically different for the pig slurry from the control treatment.

4 | DISCUSSION

The effectiveness of reducing ammonia emissions from the three slurries (biogas, cattle, and pigs) as a result of the different additives varied

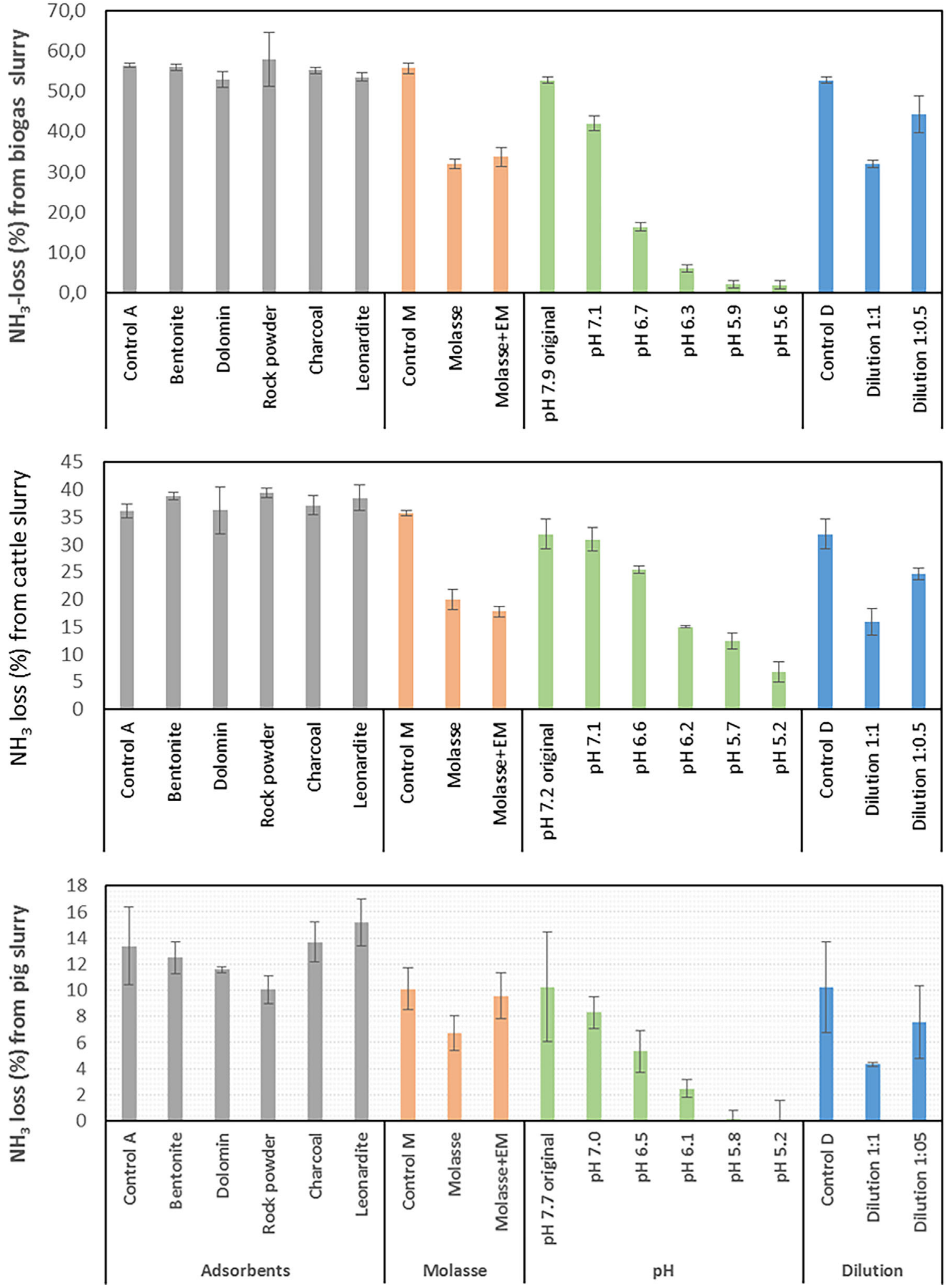

FIGURE 2 Ammonia losses from biogas, cattle, and pig slurries as influenced by adsorbents, molasses ± effective microorganisms (EM), pH, and dilution. The control treatments receiving no additives were A, M, pH original, and D. Standard deviations are indicated.

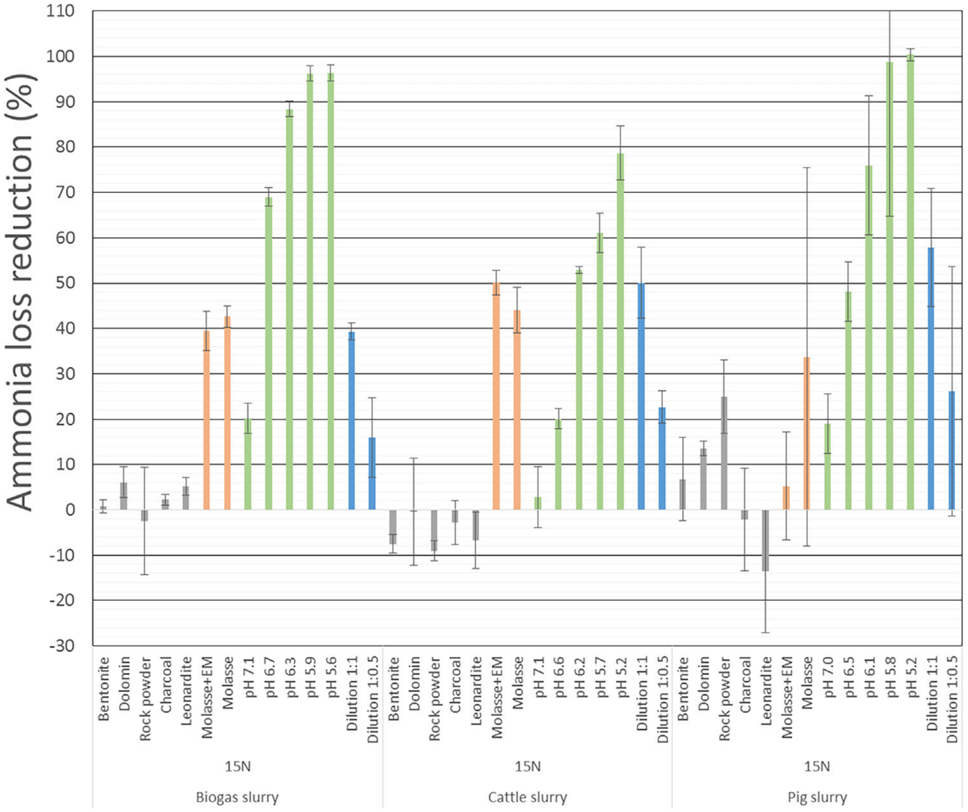

FIGURE 3 Ammonia loss reduction by additives added to biogas, cattle, and pig slurries. Sulfuric acid was used to decrease the pH. Standard deviations are indicated. EMs, effective microorganisms.

markedly. Although the ammonia losses from the three slurries differed markedly, and in decreasing order for the three slurries (biogas, cattle, and pig), the additives showed comparable effects in the slurries tested.

Regarding the size of ammonia abatement, it was most pronounced by the strongest reduction in pH values with sulfuric acid (Figure 3). At less decreased pH values exerted by sulfuric acid, a similar level of reduction was achieved compared to molasses, molasses and effective microorganisms, and a 1:1 dilution. The effective microorganisms did not further reduce ammonia losses. The group containing inorganic and organic adsorbents did not decrease or only slightly decreased ammonia emissions.

In the following, we discuss separately the effects observed in the three experiments and compare them with findings from literature.

4.1 | Experiment 1 (adsorbents)

No marked differences were observed between our study's adsorbents, mineral surfaces, and biochars; however, positive results have been reported in other literature for adsorbents. Zeolites, which are aluminosilicate minerals, are commonly used as commercial adsorbents and ion-exchange media because of their high absorption capacities of ammonium (Wijesinghe et al., 2016). These authors found that the initial NH_4^+ concentration, temperature, reaction time, and pH of the high-strength aqueous solution significantly affected the NH_4^+ adsorption capacity. However, the maximum adsorption capacity of Australian zeolites was lower than that of many other sources. They suggested that detailed investigations are required to determine zeolites' practically achievable NH_4^+-N removal potential for applications in complex media such as animal manure slurries.

Because of its high adsorption capacity, the use of biochar to capture NH_4^+-N from wastewater has become a central focus in environmental remediation studies. Kizito et al. (2016) evaluated slowly pyrolyzed wood and rice husk biochar for the adsorption of ammonium nitrogen from an anaerobic digestate slurry of piggery manure in batch equilibrium and kinetics experiments. For both biochars, ammonium adsorption increased with contact time, temperature, pH, and NH_4^+-N concentration but decreased with particle size. Ye et al. (2022) showed that biochar derived from cattle manure at 600°C showed a high nitrogen recovery in batch experiments with anaerobic digested slurries. Pereira, Perdigão, Marques, et al. (2022) found a 20% reduction in the biochars Agroforestry and Elderberry (wood shavings and stalks of cardoon pyrolyzed in a muffle furnace at 900°C) during short-term storage of pig slurry in Kilner jars. In a similar experiment, Pereira, Perdigão, Tavares, et al. (2022) also found that the NH_3 emissions were reduced by 36% with the addition of biochar (5%, w/w) or clinoptilolite, which could be related to the saturation of the adsorption capacity of NH_4^+ by biochar or clinoptilolite. Szymula et al. (2021) tested natural sorbents to reduce ammonia emissions from cattle feces in laboratory model studies. The most effective reduction in ammonia was achieved using biochar and a mixture of bentonite and zeolite, amounting to 42.5% and 24.6%. Overall, the literature points to more positive effects obtained with either mineral or organic adsorbents compared to only small effects observed in this study.

4.2 | Experiment 2 (molasses and microorganisms)

Lim et al. (2017) showed that pig slurry stored in a container with soluble carbohydrates such as sugar, glucose, and molasses can mitigate ammonia emissions. The sugar supplementation (0.1% [w/w] added to 120 kg pig slurry) reduced the aerial ammonia concentration by 33% on average. This result largely agrees with our findings in which a comparable reduction was obtained in pig slurry with increased molasses (5%). Lower amounts of molasses did not prove to be effective in pre-experiments.

El-Bied et al. (2023) addressed the challenge of mitigating ammonia emissions from stored pig slurry using biological additives. The effectiveness of the additives was evaluated in a dynamic chamber. The biological additive containing specific microbial strains were commercially obtained from DAB-Biotechnologia (a mixture of *Rhodopseudomonas palustris*, *Bacillus subtilis*, *Bacillus amyloliquefaciencs*, *Bacillus licheniformis*, *Nitrosomona europea*, *Nictobacter winogradskyi*, and nutritional substrate) and decreased NH_3 emission by 77%.

In line with our observations, Van der Stelt et al. (2007) observed no effect of effective microorganisms (Agri-mest, a protected trademark) on ammonia volatilization in batch experiments. Agri-mest is claimed to increase the energy available for anaerobic manure fermentation by microorganisms. Effective slurry treatment microorganisms mainly consist of lactic acid bacteria and yeasts and should enhance fermentative decomposition (Van der Stelt et al., 2007). Mateo-Marín et al. (2021) also showed that additives, including microbial activators, did not reduce ammonia emissions in field experiments involving pig slurry. Ammonia emissions were measured in semi-open static chambers after treatment applications at pre-sowing 2016 and side-dressing 2017 and amounted to 7%–9% and 19%–23% of $NH_4{}^+$-N ha^{-1}.

4.3 | Experiment 3 (pH and dilution)

El-Bied et al. (2023) demonstrated that for stored pig slurry in open lagoons acidified to pH 5.5, ammonia emissions could be reduced by 99% with sulfuric acid. This compares well with our study, where a 99% reduction in ammonia emission was achieved with pH 5.8 for surface-applied pig slurry.

Pereira, Perdigão, Marques, et al. (2022) observed a 58% reduction by acidification with concentrated sulfuric acid to pH 5.0 of short-term stored pig slurry. A photoacoustic multigas monitor was used to measure the ammonia emissions. In a similar experiment, Pereira, Perdigão, Tavares, et al. (2022) found that the NH_3 emissions were reduced by 51% by adding alum, which could be attributed to maintaining a stable pH of 5.0.

Regueiro et al. (2016) investigated an alternative to sulfuric acid for decreasing ammonia volatilization. In closed vessels during a 60-day storage period, they observed that sulfuric acid reduced ammonia emissions at pH 5.5 by 75% in pig slurry and 81% in dairy slurry, and alum by 69% in pig slurry and 87% in dairy slurry. In our study, ammonia emissions were strongly reduced in pig slurry and slightly less reduced in cattle slurry at similar pH values. Using dynamic chamber measurements on 1-m^2 plots, Owusu-Twum et al. (2017) showed that the loss of a liquid cattle slurry fraction was reduced by 93% using sulfuric acid to decrease the pH to 5.5. We used the whole slurry compared to their experiment, which most likely explains the authors' more efficient emission reduction. In their experiment, losses from the whole slurry were ∼39%, compared to 17% for the liquid fraction.

Losses from the 1:1 diluted slurry were approximately halved. This is an efficient method, but it entails doubling the volume that must be distributed. It is still economical when fields are no further than 5 km away; alternatively, larger slurry tanks are required.

It must be remembered that most of the other experiments cited from the literature were conducted under laboratory conditions simulating slurry storage. Whether these results can be extrapolated to the field application of slurries needs to be shown.

The proposed technique is not restricted to small soil-filled containers. This ^{15}N mass balance technique has also been used to investigate ammonia losses from grass sods contained in larger couplers (diameter 15.2 cm) placed in grass stands during the emission period. The technique has further been tested in grass plots (13.2 or 12.5 m^2 in size) on which different slurry applicators were used (trailing hose, trailing shoe, and slot injector). Soil grass sods were removed using a grass sod cutter (30 × 22 cm and 6–12 cm deep). The preparation of these larger samples was much more laborious due to larger volume that had to be handled, especially when several replicate soil-grass samples were taken from a plot. It is essential to adapt the sampling depth to the infiltration depth, that is, shallower with broadcasting and deeper with injection, which should be determined beforehand.

Harper (2005) indicated that using N isotopes to estimate NH_3 loss may be permissible if there is no plant activity for absorption and desorption. It has been seen that ammonia losses from slurry occur within 48 h; there seems to be no restriction to applying this method to detect losses from applying slurries either to bare soil or cropped soil, preferably with shorter crop stands.

One advantage of the proposed method is its precise applicability. We compare this for a plot slurry applicator which demonstrated a coefficient of variation of 5.3% between different trailing hoses. This relatively small value will, however, increase with agricultural slurry applicators in field applications or the manual use of watering cans used for plot experiments, showing a more significant variation in their distribution. In our experiments with intensive mixing of the slurry and cutting by a vortex cutter, losses might have been somewhat smaller than those observed with on-farm slurry distributors using cutters; however, our procedure was likely more effective in mixing and cutting.

Besides ammonia, other possible nitrogen losses, such as N_2O and N_2, are small in the short term, which is 48 h. Buchen-Tschiskale et al. (2023) found that after 60 days, regardless of the application (trailing hose or slot injection), N_2O losses reached 0.1 kg N_2O-N ha^{-1}, while N_2 emissions reached up to 3 kg N ha^{-1}.

5 | CONCLUSIONS

Additives can serve to conserve nitrogen, but as can be observed in this study, the results can be pretty variable. The investigated adsorbents were ineffective in mitigating ammonia losses, while mixed results exist in the literature, pointing to the possibility of preserving nitrogen with chemical adsorbents such as minerals or organic materials. The results indicate that locally available products must be tested before usage is recommended to farmers.

Positive results were obtained for acidifying substances such as sulfuric acid. As several risks are associated with the use of this strong acid, alternatives should be studied to protect the health of farmers and animals. The results also show that depending on the slurry type, different amounts of sulfuric acid are required.

In agreement with the literature, molasses facilitated the reduction of pH and may be an alternative for farmers near sugar beet factories. Alternative food industry products can also serve this purpose.

No positive results were obtained by adding microorganisms in this study, and the literature outlines both negative and positive results. Further intensive research is therefore required to validate such products.

In addition to the possibility of increased infiltration, dilution (1:1) with water was effective. This can be relatively cost-effective when rainwater is collected on-farm.

The ^{15}N mass balance technique allowed us to precisely determine ammonia losses from surface-applied slurries containing many different additives. This method is a standardized technique allowing for investigating a broad range of additives, promising decreased ammonia losses and conserving nitrogen. The new method allows for the quantitative determination of ammonia losses as verified in previous experimentation and can also serve as a standard comparison technique for other ammonia measurement techniques.

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