Laboratory case/control test of three additives on their reduction of NH_3 and CH_4 emissions from dairy cow manure

MEET-ID RAPPORT 2022-001

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PREFACE

Wageningen Livestock Research (WLR) is performing a project focussing on measures to reduce methane (CH_4) emissions in the dairy sector. The project is conducted within the national research programme 'Climate envelope'. In collaboration with Centrum Landbouw en Milieu (CLM), Monteny Environmental Consult, Meet-ID and Biont Research to perform a case/control laboratory experiment using vessels under controlled conditions to measure the methane and ammonia (NH_3) reduction potential of 3 commercially available slurry additives. This report presents the methodology and results of this study. For the methodology, recommendations from a previous comparable experiment were incorporated.

Meet-ID would like to acknowledge WLR and the Ministry of Agriculture, Nature and Food Quality for the contract and the additive suppliers for the fruitful collaboration.

Summary

As a sequel to a previous case/control laboratory experiment on the NH_3 and CH_4 emission reduction potential of 3 additives to dairy cow slurry (Monteny *et al*. 2021), Meet-ID has performed a second, similar experiment with 3 different additives. The methodological improvements suggested after the previous experiment have been implemented, most importantly: 1) similar air flow for sampling of the headspaces; 2) use of a climate controlled facility; 3) improved management of the slurry to assure equal slurry composition in each vessel.

The additives investigated are BioAktiv, No-CH (a combination of water and $MgCl_2$) and SOP Lagoon. Sulphuric acid was applied as positive control.

The relative emissions of NH_3 and CH_4 were as follows

	Relative emission [%]	
Treatment / additive	**NH_3**	**CH_4**
No-Ch (water + $MgCl_2$)	63	72
BioAktiv MZ	104	98
SOP-Lagoon	100	91
Sulphuric acid	10*1)	94*1
Reference manure	**100**	**100**

*1) calculated based on data as of 8 November.

Emission reductions of Bioaktiv and SOP Lagoon were negligible, which was contrary to expectations.

The No-Ch additive (water + $MgCl_2$) reduced NH_3 and CH_4 in this experiment, namely with 37% and 28% respectively. The NH_3 reduction is expectedly a combination of dilution with water (1.68 / 12 = approximately 14%, assuming a linear relationship between rates of dilution and emission), and the remainder (37 – 14 =) 23% reduction being related to formation of struvite.

The emission reduction of sulphuric acid were according to literature, whereas for CH_4 also greater reductions are reported.

Inhoud

1. Introduction

Wageningen Livestock Research (WLR) is performing a project focussing on adaptation of barns in dairy husbandry to abate methane (CH_4) emissions in the framework of a national research programme. Since multiple gaseous emissions from animal husbandry need to be reduced, the impact of CH_4 emission reducing options on NH_3 emissions need to be addressed. Therefore WLR has asked Centrum Landbouw en Milieu (CLM), Monteny Environmental Consult, Meet-ID BV and Biont Research to perform a case/control experiment under controlled conditions into the methane and ammonia (NH_3) reduction potential of 3 commercially available slurry additives used on dairy cow slurry. The experiment is best characterized as a mesocosm experiment using vessels to simulate stored slurry. This report presents the methodology and results of the measurements performed between October 27 and December 13, 2021 in the laboratory Meet-ID in Lemelerveld, the Netherlands.. For the methodology, recommendations from a previous comparable experiment (Monteny *et al.* 2021), were incorporated: 1) similar air flow for sampling of the headspaces; 2) use of a climate-controlled facility; 3) improved management of the slurry to assure equal slurry composition in each vessel.

2. Material and method

2.1 Test setup

The test setup consisted of perspex vessels (h 58.5cm, d 23.5 cm) containing equal amounts of homogenized dairy cow slurry (figure 1b). Each vessel is connected to a sampling array allowing measurement of NH_3 and CH_4 concentrations in the vessel headspace (Figure 1a)

 Front view of the climatized container of Meet-ID with the vessels in an insulated wooden crate (on the back) measurement rack (in the front), with multi point sampler (on top), ammonia analyser (in the middle) and methane analyser (on the bottom). The duct connection block is placed on top of the measurement rack and has critical orifices in each duct for flush flow control (see Table 1).	 Arrangement of vessels with manure, lids and sampling ducts.

Figure 1. Measurement set-up with manure vessels (a) and sampling array (b).

To allow optimal headspace sampling, each vessel is covered with a lid having 12 evenly distributed inlets (3 mm diameter each), and a central sampling point (see figure 1b). Sampling points were connected to the sampling array by 500 cm long 1/8 inch PTFE tubing. To optimise headspace mixing, the lids possessed a central protrusion (9 cm long / 5 cm wide) on the inside of the lid, separating the sampling point from the inlets (see Figure 2).

In the sampling array, a multipoint sampler controlled the sequence and duration of vessel headspace sampling. Headspaces were continuously flushed with an atmospheric turnover of 16-28 times per hour (Table 1).
As is shown in Figure 1 the vessels and the measurement equipment were placed in a climate-controlled (15 ^{o}C and 70% RH) laboratory on the site of Meet-ID in Lemelerveld (The Netherlands).

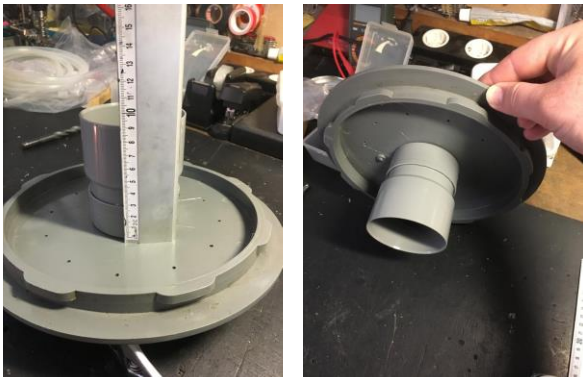

Figure 2. Vessel lids with inner protrusion to optimize headspace mixing

For the purpose of this experiment, 10 vessels were loaded each with 12 kg of dairy slurry, leaving a headspace of ~15 l. The slurry contained in each vessel is either treated with additives (‘case’) or left untreated (‘control’). The principle of this setup is described in Groenestein *et al*. (2006), who used it for exploration of the various emission sources in sow barns.

2.2 Sampling array

A 15-channel multi point sampler (see Figure 3) is used for sampling of the headspaces. A 16 Liter /minute PTFE coated double headed pump is connected to a connection block to provide continuous orifice-controlled flushing of all headspaces (see Table 1 for flow rates per vessel).

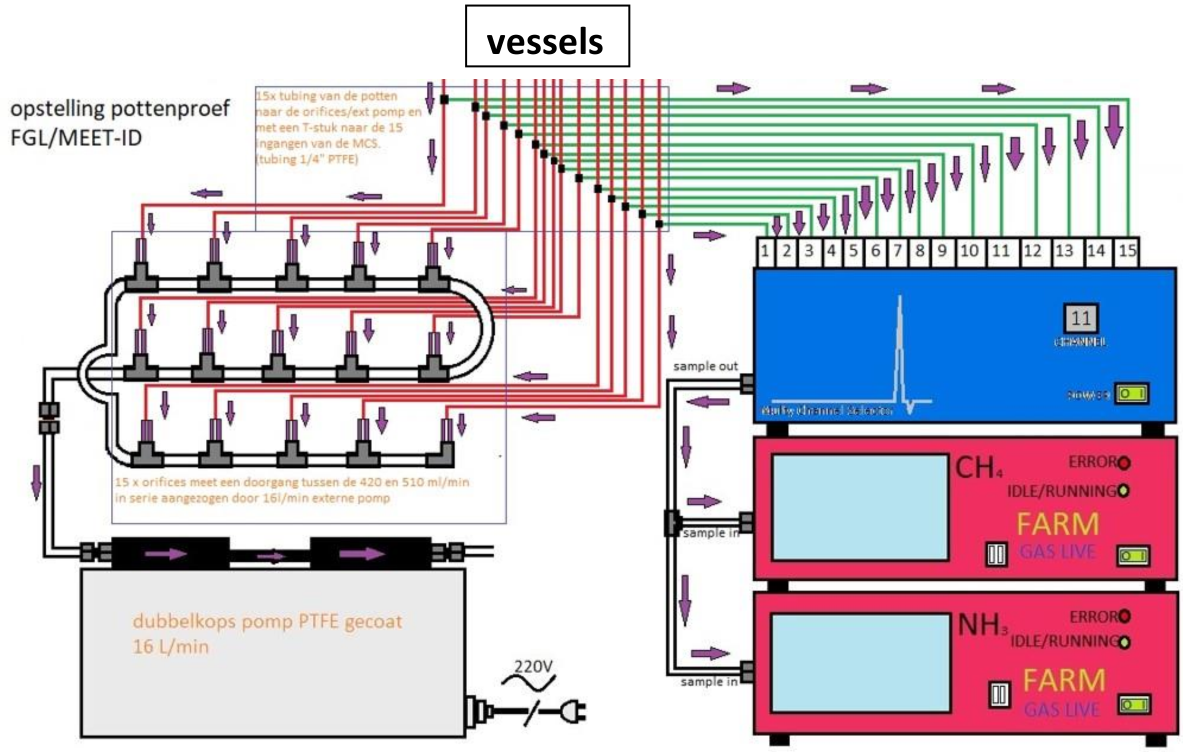

Figure 3. Schematic overview of the sampling array, critical orifices and pump (grey), multi point sampler (blue), CH_4 and NH_3 monitors (red) with an internal pump with a capacity of approximately 60 mL/minute.

An overview of the treatments is presented in Table 1.

Table 1. Overview of vessels, treatments, flush flow per vessel in Liter per minute, and atmospheric turnover of the head space air volumes.

Vessel	Treatment	Flush-flow (measured on 24 September) – L/min	Atmospheric turnover of headspace (h^{-1})
1	BioAktiv	0.512	23.4
14		0.428	28.1
2	Control	0.770	15.6
13		0.466	26.9
3	No-Ch ($MgCl_2$) + water	0.490	24.5
12		0.458	20.7
4	SOP-Lagoon	0.525	22.0
11		0.451	26.6
7	Sulphuric acid (50%)	0.556	21.6
8		0.523	22.9
15	Ambient (laboratory) atmosphere	0.522	23.0

For the sampling we aim to create similar conditions as much as possible. Concerning the flush flow (of the headspace), this is obtained by using ‘critical orifices’ in the sampling station (‘block’). However, these orifices appear to differ slightly (normal distribution) when we checked air flows. The sampling flow was the same for all vessels.

Inside the multi point sampler a switching valve allows air from a consecutive measurement of the attached vessels. The working principle of the switching valve is shown in figure 4. A single vessel is connected to the selected stream outlet, which connects to the gas monitor array. Vessels that are not measured are connected to a common outlet. The ‘selected stream outlet’ is the channel (vessel) that is actually measured (‘sample flow’).

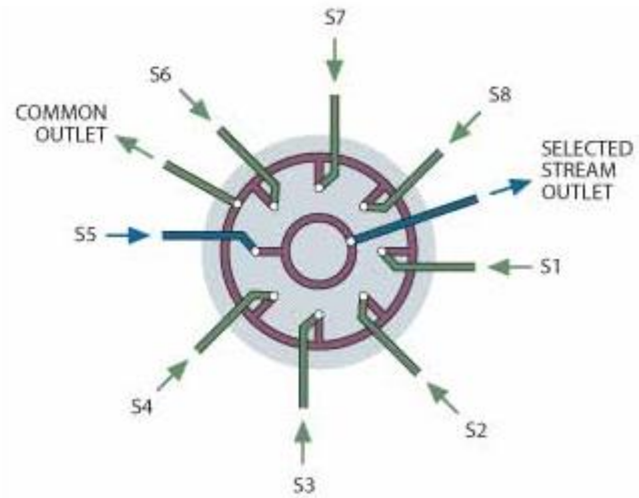

Figure 4. ‘switching valve’ applied in the multi-channel selector (example with 8 positions). (source: vici.com).

We used photo acoustic analysers (manufacturer: LSE/Synspec Groningen; see Appendix A) provided by Farm Gas Live BV for the measurement of NH_3 and CH_4 concentrations of air from the headspaces and air inside the container. The internal pumps of the analysers (60 mL/minute) were used for the measurement of the CH_4 and NH_3 concentrations in the sampled air of each vessel/headspace.

Ammonia concentrations in the headspaces were not corrected for NH_3 concentrations inside the laboratory, since for NH_3 the equilibrium concentration in the headspace is measured. For CH_4 the results presented are the difference in CH_4 concentration between each headspace and air inside the laboratory.

2.3 Treatments

Approximately 1 m^3 of freshly collected dairy cow slurry from a commercial farm in Noord-Brabant was delivered to Meet-ID on Tuesday 21 September and stored in a shadowed place on site. On Tuesday 19 October, the content of the plastic container was homogenized during 30 minutes with a concrete mixer (see Figure 5). On that day, the homogenized slurry was discharged into a 65 Liter buffer bucket and from this bucket portions of 2 Liter each were brought into each vessel until a total weight of 12 kg (Liter) slurry per vessel was reached. This was checked using an electronic weighing device (See Figure 5). This strategy was designed to maximize the comparability of the slurry composition in each vessel prior to administering the additives.

The measurements started on 19 October and after the lids were closed and were ended on 13 December.

Table 2. Chemical composition of the slurry in the vessels at the end of the experiment.

Vessel	Component	totaal-N	ammonium-N	totaal-P	Kalium	droge stof	as	pH
	Norm for analysis	WI 4.25-115	WI 4.25-103	WI 4.25-116	WI 4.25-122	WI 4.25-111	WI 4.25-112	WI 4.25-113
	Unit	g/kg	g/kg	g/kg	g/kg	g/kg	g/kg	
1	BioAktiv	4,42	2,55	0,71	4,41	86,3	27,3	8,5
2	Control	4,47	2,55	0,67	4,75	76,3	23,1	5,5
3	No-Ch	3,93	2,30	0,56	3,77	80,2	25,1	8,2
4	SOP-Lagoon	4,48	2,58	0,69	4,36	77,6	23,2	8,4
7	Sulphuric acid	4,73	2,89	0,67	4,47	84,1	28,7	7,6
8	Sulphuric acid	4,65	2,82	0,74	4,38	82,4	28,2	7,7
11	SOP-Lagoon	4,71	2,59	0,71	4,41	77,1	23,1	8,6
12	No-Ch	3,92	2,30	0,59	3,90	81,4	26,2	8,2
13	Control	4,47	2,62	0,66	4,44	80,7	24,6	8,4
14	BioAktiv	4,28	2,49	0,65	4,31	77,9	26,3	8,4

Figure 5. Homogenisation of dairy cow slurry in a 1 m^3 (container ('IBC' left hand side) and discharge of slurry in a 65 Liter buffer bucket (right hand side). The electronic weighing device is located in the red circle in the photo on the left hand site.

The height of the slurry level in each vessel was approximately 30 cm, leaving a (58.5 – 30 =) approximately 30 cm high headspace in each vessel, with a volume of (25.37 – 12 =) approximately 12 Liter.

Except for vessel #14 (untreated slurry; control), the atmospheric turnover was comparable between 20 and 28 times per hour and comparable to the turnover reported by Groenestein *et al*. (2016).

All treatments (1 replication per treatment) were performed by the manufacturers, except for SOP Lagoon and sulphuric acid. These treatments were performed by Meet-ID staff.

Two doses of 25 g of the additive 'BioAktiv MZ' were applied per vessel and stirred during a few minutes using a paint mixer.
The working principle of 'BioAktiv MZ' is thought to be based on microbial growth, whereby ammonium is used for microbial protein assimilation. Previous in-situ case/control measurements performed in the Czech Republic (Jelinek, 2012) showed a 27% reduction of pig slurry treated with BioAktiv against untreated pig slurry.

Agri Minerals applied 1.68 Liter of water and 400 g of their additive 'No-Ch' (MgCl2) per vessel, after which the content was stirred using a paint mixer. The combination of water and additive was used to simulate the application in commercial barns with concrete slatted floors and slurry storage beneath, where spraying robots are used to spray both liquids over the (fouled) floor surface area. Both liquids will eventually be discharged to the slurry pit beneath the floor and mixed with the stored slurry.
The effect of this treatment is dilution (water), whereas $MgCl_2$ is known to form 'struvite' a complex of magnesium, ammonium and (-ortho-) phosphate present in the slurry. This lowers the concentration of free NH_3 in the slurry and consequently the NH_3 volatilization from the slurry to the headspace.

The third additive SOP Lagoon consist of calcium dihydrate, that is thought to 'boost' certain microorganisms that abate the formation of harmful gases in animal manures. An amount of 1,0 g was applied per vessel and stirred using a paint mixer.

Finally sulphuric acid (50%; Breustedt Chemie Apeldoorn, Netherlands) was used as a positive reference. A [pre-ordered (based on an anticipated pH of around 5) amount of 100 g of sulphuric acid was applied per vessel under stirring, This treatment was performed on November 8 due to late delivery because of Covid-19.

2.4 Collection, processing and analysis of data

Gas concentrations of manure vessel headspaces were determined every 15 hours after an initial equilibration period of 4 days. This resulted in a maximum of 73 data points per vessel over the incubation period of 51 days, collected at different times of day throughout the incubation.

Each individual concentration data-point is determined from an hour-long measurement procedure consisting of flush-phase and a measurement-phase. The flush-phase serves to reach equilibrium in the system and lasts 16 minutes for NH_3 and 50 minutes for CH_4. During the measurement phase, the monitor generates individual concentration estimates every 58 seconds. The median of these estimates is to represent the headspace concentration over the measurement-procedure.

Following collection of data, relative emissions of NH_3 (RE_NH3) and CH_4 (RE_CH4) are calculated for each vessel x:

$$RE\_NH3_x = \frac{\overline{[NH3]_x}}{\overline{[NH3]_r}} * 100\%$$

$$RE\_CH4_x = \frac{\overline{[CH4]_x} - \overline{[CH4]_{in}}}{\overline{[CH4]_r} - \overline{[CH4]_{in}}} * 100\%$$

With $\overline{[NH3]}$ and $\overline{[CH4]}$ the average concentrations of ammonia and methane in ppb, measured in the target vessel (x), reference vessel (r) and the atmospheric inflow of the vessels (in). Note that only CH_4 emissions are corrected for inflow from the ambient atmosphere, as it is assumed that the equilibrium NH_3(ag) NH_3(g) is not influenced by the inflow concentration.

3. Results and discussion

Figures 6 and 7 show the development of the CH_4 and NH_3 headspace concentration, respectively, for each treatment and the air inside the laboratory.

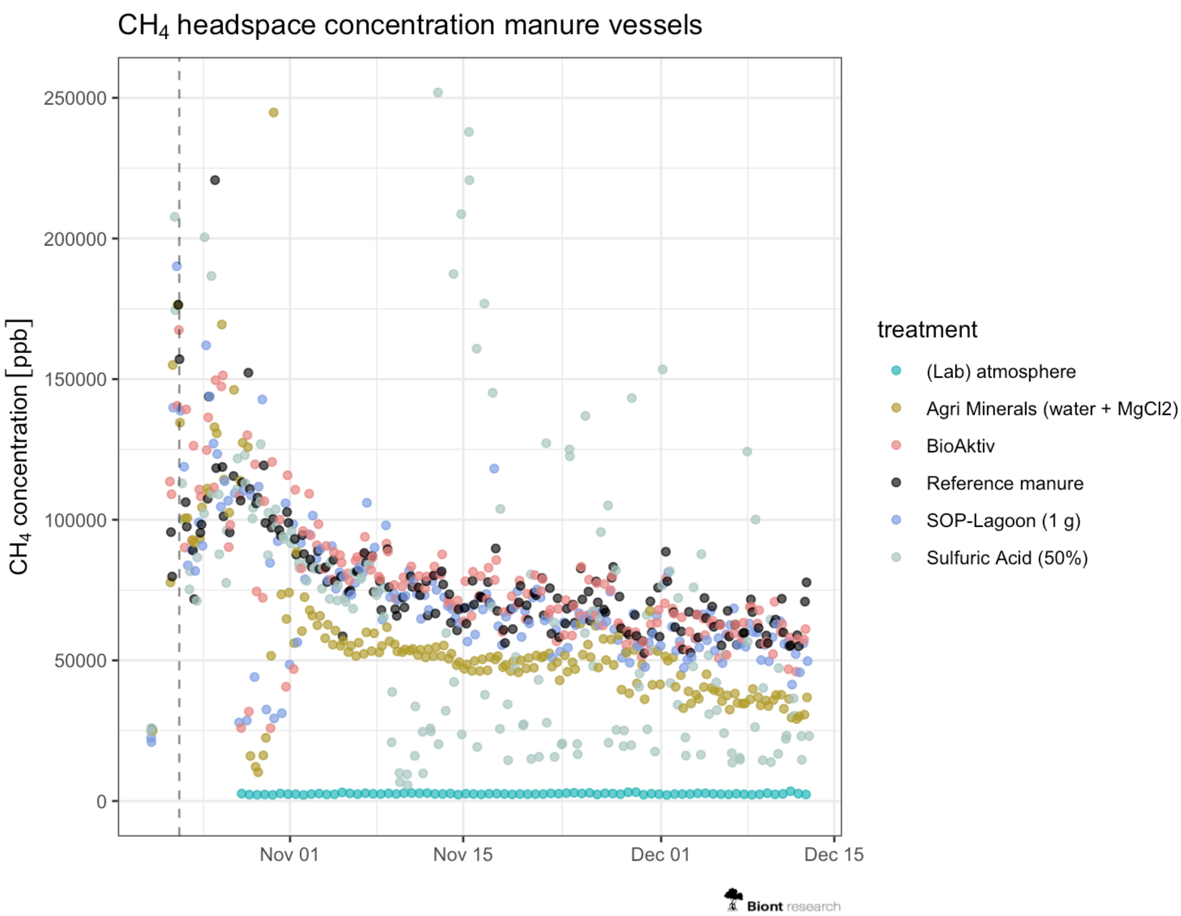

Figure 6. CH_4-concentration (ppb) in the headspace of each manure vessel and the ambient (laboratory) atmosphere used to flush the headspaces. The horizontal (dotted) line indicates the moment start of the measurements 19 October. Note 'Agri Minerals' is No-Ch + water).

The emission reducing effect of the combination of No-Ch and water ('Agri Minerals') and of sulfuric acid is clearly visible and the most pronounced.

Sulpheric acid was applied on 8 November. This event Is clearly visible in the 'restless' pattern of the concentrations, which were independent of the vessel.

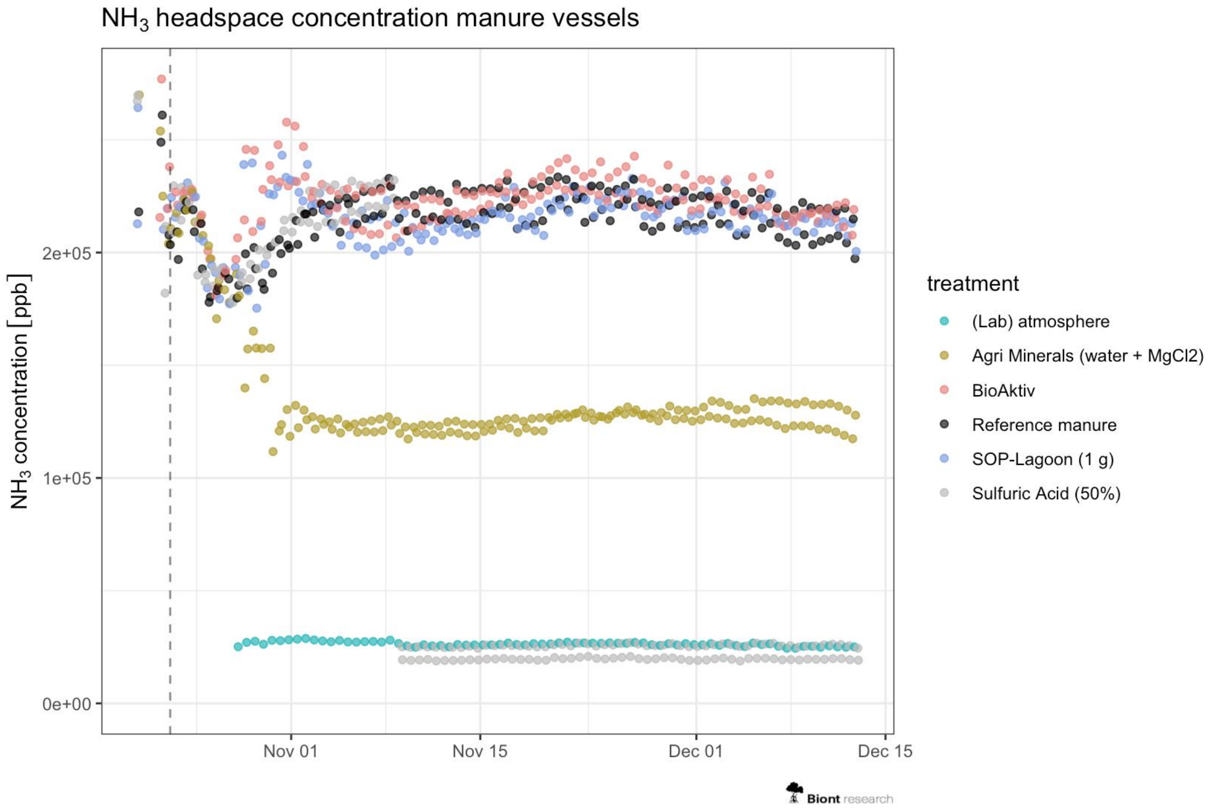

Figure 7. NH_3-concentration (ppb) in the headspace of each manure vessel and of the ambient (laboratory) atmosphere used to flush the headspaces. The horizontal (dotted) line indicates the moment start of the measurements 19 October. Note 'Agri Minerals' is No-Ch + water). Furthermore, sulphuric acid was applied on 8 November.

Also for CH_4, the emission reducing effect of No-Ch and sulphuric acid are clearly visible in this figure. Table 2 summarizes the average relative emissions of NH_3 and CH_4 per additive, calculated as the relative difference of the gas concentrations with the untreated slurry (reference).

Table 2 shows the average (n = 2) relative NH_3 and CH_4 emission per additive/treatment.

Table 2. Average relative NH_3 and CH_4 emission per additive/treatment.

	Relative emission [%]	
Treatment / additive	**NH_3**	**CH_4**
No-Ch (water + $MgCl_2$)	63	72
BioAktiv MZ	104	98
SOP-Lagoon	100	91
Sulphuric acid	10 *1)	94*)
Reference manure	**100**	**100**

1) calculated as of 8 November.

Only the No-Ch (water + $MgCl_2$) reduced NH_3 and CH_4 in this experiment with 37% and 28% respectively. The NH_3 reduction is expectedly a combination of dilution (1.68 / 12 = approximately 14%, assuming a linear relationship between rates of dilution and emission), and the remainder (37 – 14 =) 23% being related to formation of struvite. The CH_4 reduction is possibly related to differences in settling or floating of slurry solids (organic matter) between the case and the control.

Contrary to the expectations of the manufacturers, BioAktiv and SOP Lagoon showed no reduction in this experiment. In literature (Jelinek, 2012) a 27% reduction of NH_3-emission was reported when the additive was applied in a pig barn.

The SOP Lagoon website (www.solarimpulse.com) mentions that "the application of the product can reduce the emissions of methane up to 23%, of CO_2 up to 22%, N_2O up to 100% and NH_3 up to 100%". Furthermore, Peterson *et al.* (2020) reported emission reductions for CO_2, CH_4, N_2O and NH_3 by 14,7%, 22,7%, 45,4% and 45,9%, respectively.

The data on slurry composition at the end of the measurements (Table 2) show an on average consistent composition where the effect of treatments were clearly visible, e.g.:

- pH of both sulpheric acid treatments was markedly lower
- reduced NH_3-emission of sulpheric acid resulted in higher total-N and ammonium-N concentrations since less ammonia was lost
- Similarly, also No-Ch showed higher total-N and ammonium-N concentrations which is consistent with the NH_3 reduction measured
- No-Ch resulted in a slightly higher dry matter and ash content as a result of adding of salts

The dosages of the additives in this experiment and practice were as follows, showing no or small difference between de dosage used and advised (for No-Ch and BioAktiv).

Table 3. Dosage per additive in this experiment compared to dosage information for use on commercial dairy farms.

	This experiment	On commercial farms
No-Ch (g)	400 = 3 % (w)	Same as in experiment
BiaAktiv MZ (g)	2x 25 = 50 g= 0.4% (w)	2 kg BioAktiv MZ on 100 m^3 of cow slurry or 2 g per cow per day (via diet)
SOP Lagoon (g)	1 = 0,008 % (w)	No information

The addition of sulphuric acid to pH 5 reduced NH_3 with 90%, which is according to literature on Dutch conditions (e.g Bussink and Van Rotterdam-Los, 2011). The reduction of CH_4 was markedly lower (6%). Since the sulphuric acid was pre-ordered to achieve pH 5, it is well possible that the buffer capacity of the slurry lead to a pH increase after dosage of 100 g per vessel and mixing stopped. The relatively reduced reduction when compared to NH_3 is in accordance with findings reported by Volokov *et al.* (2021) who found that similar reductions for CH_4 requires up to 4 times more acid when compared to NH_3.

4. Conclusions

As a sequel to a previous case/control laboratory experiment on the NH_3 and CH_4 emission reduction potential of 3 additives to dairy cow slurry (Monteny *et al*. 2021), Meet-ID has performed a second, similar experiment with 3 different additives. The methodological improvements suggested after the previous experiment have been implemented, most importantly: 1) similar air flow for sampling of the headspaces; 2) use of a climate controlled facility; 3) improved management of the slurry to assure equal slurry composition in each vessel.

The additives investigated are BioAktiv MZ, No-Ch ($MgCl_2$) in a combination with water and SOP Lagoon. These additives are potentially able to reduce CH_4 and NH_3 emissions, either based on literature or theoretical considerations.

Emission reductions of Bioaktiv and SOP Lagoon were negligible, which was contrary to expectations.

The No-Ch additive (+water) reduced NH_3 and CH_4 in this experiment, namely with 37% and 28% respectively. The NH_3 reduction is expectedly a combination of dilution with water (1.68 / 12 = approximately 14%, assuming a linear relationship between rates of dilution and emission), and the remainder (37 – 14 =) 23% reduction being related to formation of struvite.

The emission reduction of sulphuric acid were according to literature, although for CH_4 also greater reductions are reported.

Literature

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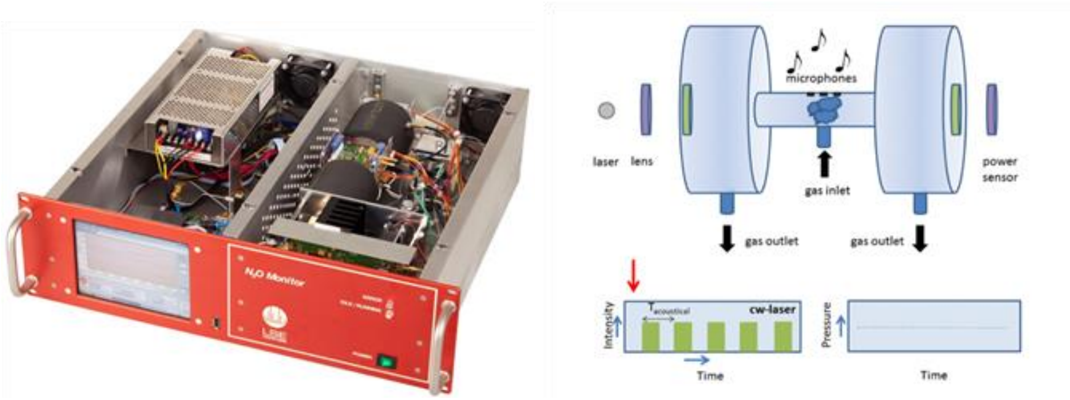
Appendix A. Foto-acoustic analyser (in Dutch)

De monitoren (analyzers) maakt gebruik van fotoakoestiek met behulp van een telecomlaser voor het meten van de concentratie ammoniak. Het laserlicht wordt omgezet in een geluidsgolf die wordt opgevangen door enkele microfoons. De golflengte van het laserlicht is specifiek voor het type gas dat daarbij gemeten wordt. Schematisch weergegeven ziet dit er als volgt uit:



Figuur A1. *LSE-monitor voor NH_{3}- en CH_{4}-concentratiemetingen.*

De gegevens kunnen op afstand worden ingezien met behulp van Teamviewer. Tevens kunnen op afstand de gegevens worden uitgelezen en gelogd.