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Effects of SOP Lagoon Additive on Gaseous Emissions from Stored Liquid Dairy Manure

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Abstract: Animal manure is a source of greenhouse gas (GHG) emissions and other pollutants and nuisances such as ammonia and odors. There are several technologies to reduce emissions on animal farms including manure additives; however, few have been proven effective and easy to apply to dairy lagoon systems. The present research aimed at testing the ability of the commercial additive "SOP LAGOON" to reduce emissions of GHGs (i.e., carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O)), as well as ammonia (NH_3) and odors from lagoon stored liquid manure. Emissions of GHGs, NH_3 and odors were measured in the laboratory from barrels filled with 65 L of manure treated with SOP LAGOON or left untreated as a control. Manure was collected from a commercial dairy that is located in Solano County, California. Emissions of GHGs and NH_3 were continuously measured for one week using flux chambers placed on top of the barrels and connected to a mobile air emissions laboratory. The effects of the untreated control, versus the two respective treatment additive doses of 30.8 and 61.6 g/m^3 of manure were compared to each other. The low dose was selected based on the manufacturer recommendation and the high dose was selected by doubling the low dose. Results showed that SOP LAGOON applied at the high dose (61.6 g of SOP LAGOON per m^3 of manure) versus the control greatly reduced ($p < 0.05$) emissions of CO_2, CH_4, N_2O and NH_3 by 14.7%, 22.7%, 45.4% and 45.9%, respectively. Furthermore, the high dose of SOP LAGOON treated samples versus the control samples showed less odor intensity ($p < 0.05$). There was no significant effect of the low dose of SOP LAGOON on the emissions of different gases. The HIGH dose of SOP LAGOON might decrease the number of methanogens and hydrolytic microorganisms and their excreted enzymes during manure storage. Further studies are needed to investigate the mechanism of emission reduction using SOP LAGOON.

Keywords: sustainability; SDG; GHG; ammonia; odor; dairy; liquid manure; manure additive

1. Introduction

The international community has increased awareness of air pollutants and greenhouse gas (GHG) being emitted from agriculture, including animal husbandry. The three major anthropogenic greenhouse gases are carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). The IPCC estimated that agriculture contributes about 24% of GHG emissions from anthropogenic sources globally in 2010 [1], and about 9% in the US [2]. While animal agriculture is largely omitted from

CO_2 inventories, the industry is a major source of CH_4 and N_2O that have global warming potentials 25 and 298 times greater than CO_2, respectively [3], when calculated on a 100-year time span. More recently, the new Global Warming Potential (GWP*) was proposed, which recalculates the impact of methane taking into account the shorter lifespan of this gas in the atmosphere [4]. The proposed value for methane's warming potential is 84 times that of CO_2, implying that changes in these emissions have a greater impact on the climate than what was previously estimated. In addition to GHGs, the livestock sector is a major source of other air pollutants (e.g., NH_3) that negatively affect air quality. Although ammonia is not a GHG, it is considered a secondary source of N_2O due to its re-deposition on the land [5].

Air pollutants from animal farms are harmful in their original form and can be precursors in the formation of criteria pollutants. For instance, ammonia can cause eutrophication, acidification and disturbance of natural ecosystems after its deposition, and can also be a precursor of fine particulate matter, $PM_{2.5}$ [6]. Wu et al. [7] highlighted the correlation between $PM_{2.5}$ formation and the presence of ammonia (NH_3) in the air, identifying the gas as having a crucial role in the nucleation of these particles. While GHGs are heat-trapping and more of a mid- to long-term challenge, air pollutants can create immediate health issues including respiratory issues such as asthma and pneumonia. The American Lung Association [8] indicated that 8 of the 11 cities with the highest year-round concentration of particulate matter, especially fine $PM_{2.5}$, were located in California, largely due to the state's transportation and agricultural sectors.

Approximately 10% of the global GHG emissions from agriculture are produced from livestock manure management, contributing an equal proportion to the US methane emission inventory [9]. In California, anaerobic lagoons are the most common strategy for manure management, and these lagoons are considered the largest source of CH_4 emissions after enteric fermentation. They can also emit large quantities of N_2O [9]. The California Air Resources Board (ARB) recently adopted the Short-Lived Climate Pollutant Strategy (SLCP) to reduce emissions of black carbon, CH_4 and other SLCPs. The SLCP included a focus on emissions of CH_4 from California dairies, particularly those contributed by waste management. Recent legislation (Senate Bill 1383) requires the implementation of the SLCP strategy by January 1, 2018. The strategy includes a 40% CH_4 emission reduction from 2013 levels by 2030 [10].

Based on the estimation of the emissions from three dairies in Idaho, Leytem et al. concluded that changes in the manure handling system may be the best way of mitigating emissions [11]. Several technologies are being applied to reduce the emissions of different gases from animal manure, including but not limited to anaerobic digestion and other alternative technologies such as solid/liquid separation. Nevertheless, the effluents of anaerobic digestion and separated liquid manure may be sources of gas emissions if not well managed. Manure additives were proposed as practical and cost-effective methods for reducing the emissions of NH_3 and GHG from dairy manure [12]. McCrory and Hobbs defined manure additives as substances that can be applied to reduce the emissions of gases and odors from livestock waste [13]. They categorized the additives used for the alleviation of NH_3 emissions as bacterial–enzymatic bio-augmentations, plant extracts, oxidizing agents, disinfectants, masking agents and adsorbents.

Although there are publications on the application of additives mitigating either CH_4 or NH_3 emissions from swine manure [14,15], only a few publications exist on the application of additives to dairy manure. Holly and Larson studied the effects of two commercial additives (More than Manure (MTM) and Pro-Act Biotech (Pro-Act)) and biochar on dairy manure composition and the resulting GHG and NH_3 emissions [16]. Neither MTM nor Pro-Act affected the solid content of manure slurry or NH_3 emissions from manure storage for 28 days. However, MTM increased CO_2 emissions. Biochar increased the total NH_3 in the manure, but it did not reduce NH_3 emissions. Additionally, biochar did not reduce the emissions of CO_2, CH_4 or N_2O. After spraying 0.5% solutions of hydrogen peroxide and potassium permanganate on the surface of liquid dairy manure, Xue and Chen observed a reduction of superficial emissions of hydrogen sulfide (H_2S) and NH_3 [17]. After inducing strong acidification of

manure with sulphuric acid, Petersen et al. observed a reduction of CH_4 and NH_3 emissions from cattle slurry [18]. Forms of gypsum as an additive to mitigate emissions from manure have also been tested in numerous studies [19–22]. The addition of gypsum has shown a reduction in NH_3 emissions during the storage and composting phases of manure, but the results on GHG have not been as clear. Li et al., Yang et al. and Hao et al. found that the addition of gypsum increased N_2O emissions, while Yang et al. also measured a decrease in CH_4 emissions [20,21,23]. A recent study by Borgonovo et al. tested the gypsum-based commercial additive, "SOP LAGOON", on fresh dairy manure and found the additive to be effective in reducing direct NH_3 and GHG emissions [24]. With the use of a Life Cycle Analysis (LCA) they also found a positive mitigation to climate change and particulate matter formation. The objective of the present study was to investigate the effect of SOP Lagoon additive on the emissions of GHGs and criteria pollutants as well as odor intensity from liquid manure (aka lagoon water).

2. Materials and Methods

2.1. Experimental Design

A completely randomized design was used to determine the effects of the two concentrations of SOP on GHG emissions, NH_3 emissions and odor intensity from lagoon water. The treatment included a control (CONT, no additive), a low dose (LOW; the addition of 2 g per barrel (30.8 g/m^3 of manure) of SOP Lagoon, following the manufacturer's instructions) and a high dose (HIGH; the addition of 4 g per barrel (61.6 g/m^3 of manure) of SOP Lagoon) applied to the lagoon water. SOP Lagoon is a commercial additive that is manufactured by SOP Srl (SOP Srl, VA, Italy). SOP Lagoon consists of calcium sulfate dihydrate (agricultural gypsum), which is processed with the company's proprietary technology. The product claim is to improve liquid manure management through inhibiting the production and release of GHGs (e.g., CH_4 and N_2O) and criteria pollutants (e.g., NH_3) while also reducing the odor intensity from liquid manure.

The experimental unit was the barrel to which the individual treatment was applied. Two replicates of each treatment were conducted over a one-week period (round). The round was then duplicated for a total of four times per treatment (n = 4) over the total two-week study period. As Borgonovo et al. (2019) showed peak efficacy at day 4 and due to the stagnant setup of the system, a one-week period was chosen for each round to test the short term efficacy of the product on liquid manure with continuous measurements over the entire test period.

2.2. Manure Collection and Experimental Setup

Liquid manure (i.e., lagoon water) was collected twice to conduct the two rounds of emissions testing over two consecutive weeks, from a 900 head commercial dairy farm in Solano County, CA. Liquid manure from the commercial farm was sampled for wet chemical analysis by Cumberland Valley Analytical Services, Inc. (Waynesboro, PA). The manure contained 0.27% solids, 99.7% moisture, 0.006% total nitrogen and had a pH of 7.8. A trash pump was used for liquid manure collection for a total of 0.757 m^3 (200 gallons) of liquid manure that was allocated into six 208 L (55 gallons) open top steel drums with lids (Uline, Pleasant Prairie, WI). The drums had a height of 0.88 m (34.5 in) and an inner diameter of 0.565 m (22.25 in). The liquid manure drums were then transported to the experiment location in a 22 m by 11 m covered enclosure building (CPE) at the Animal Science Department facilities at UC Davis. The CPE door was open during the experiment to allow for temperature and relative humidity in the CPE to more readily mirror external ambient conditions during the two experimental rounds (shown in Figure 1).
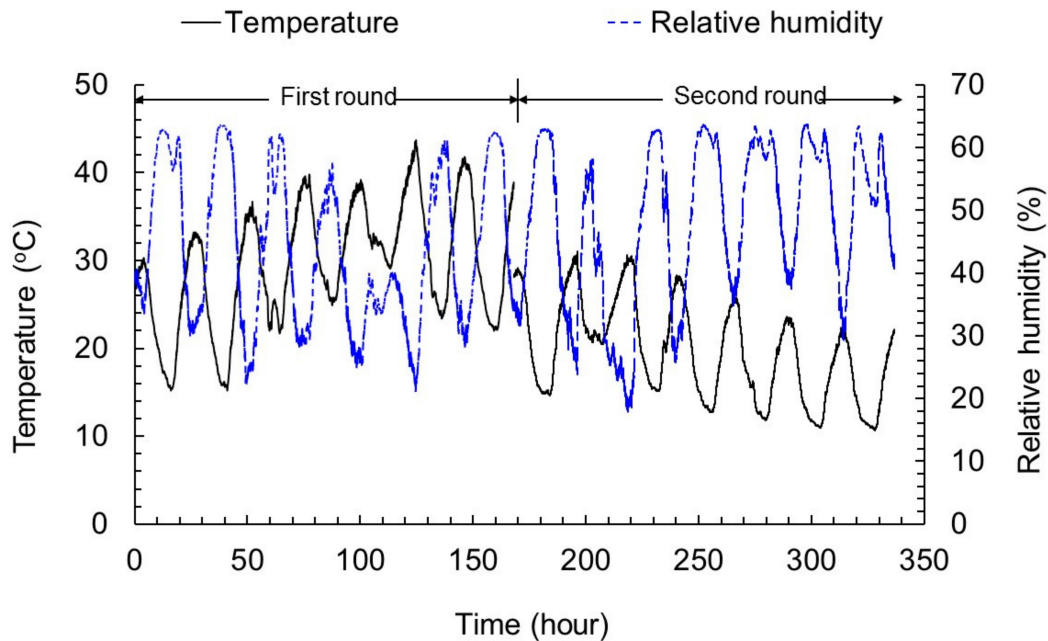
Figure 1. Average temperature and relative humidity inside the covered enclosure building (CPE) during the two experimental rounds.

After arrival at the CPE, 65 L of the liquid dairy manure was pumped out of the transport drums and into each new sampling drum, so that the quality of the manure was as homogeneous as possible among the different barrels at the start of the test, allowing for a direct comparison of the treatments. The dairy lagoon water was weighed, using a calibrated scale with an accuracy of ±2%, into each of the six drums that were used for the storage of the liquid manure over the sample period (GFK 165a Floor Checkweighing Scales, Adam Equipment Inc, Oxford, CT, USA). The drums were then relocated to the testing area, each at a distance of 1.5 m from any neighboring sample drum to prevent carryover effects.

The respective specified amounts of the SOP Lagoon treatments were weighed using a calibrated Brecknell C3235 Checkweighing scale with an accuracy of ±2% (Avery Weigh-Tronix, LLC. Fairmont, MN, USA). Treatments were added to their specified drums and each of the sample drums was then mixed for 1 min (including CONT) to ensure homogenous samples. The drums were then covered with a plywood sheet with a 0.381 m (15") diameter hole cut out of the middle and OdoFlux flux chambers (Odotech Inc. Montreal, Quebec, Canada), which were placed over the hole in the plywood to allow for air sample collection from each drum (Figure 2). The six flux chambers were made of acrylic resin and had a volume of 64.5 L, consisting of a cylindrical enclosure with a spherical top and a small hole to allow for the samples to remain at constant pressure. Real-time sampling of emission flux chambers began, and constant sampling occurred over the week testing period. The sampling protocol was then repeated for an additional round, for a total of 4 one-week replicates per treatment over the total two-week study period. It was assumed that the manure characteristics were the same over the short duration of the manure collection period therefore the number of replicates was four.

Figure 2. Emission flux chamber covering a 208 L (55 gallons) open-top steel drum containing liquid manure.

2.3. Air Sampling Using Emission Flux Chambers

The inside circumference of each flux chamber was lined with perforated Teflon tubing to allow continuous ambient airflow through the system at a rate of 8 L/min. The air flow was regulated by mass flow controllers connected to air pumps with fresh ambient air being pumped into the system from outside the sampling area (GAST, Model3HEB-69T-M345X, Benton Harbor, MI; see Figure 3). These mass flow controllers compensated for the temperature effects on air flow rate when calculating the emission rates. All other devices were operated in ambient temperature. An additional Teflon tube was attached to the top for sample extraction. The sampling tubes from the flux chambers were connected to a rotary valve. Air samples were fed into a manifold and then distributed for individual gas analysis. The flux chambers were sampled in sequence for 20 min each followed by a sampling of ambient air. The sampling cycle was repeated continuously. The concentration of different gases was measured using a continuous gas analyzer located in the mobile agricultural air quality laboratory.

2.4. Environmental Measures

Air samples were analyzed for carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and ammonia (NH_3). The GHGs (CO_2, CH_4, N_2O) and ammonia (NH_3) were measured using an INNOVA 1412 photo-acoustic multi-gas analyzer (LumaSense Technologies Inc., Ballerup, Denmark). The INNOVA 1412 analyzer had the following minimum detection limits: 1.5 ppm for CO_2, 0.4 ppm for CH_4, 0.03 ppm for N_2O and 1.0 ppm for NH_3. The maximum detection limit for the INNOVA is 10^6 ppm. To compensate for any possible water interference in the infrared region, water vapor was also measured by the INNOVA simultaneously with the other four gases. Prior to the experiments, the analyzer was factory calibrated and daily zero and span checks were performed.

All monitoring equipment was housed in a mobile agricultural air quality laboratory. In addition, the lab included a computer system to control sample timing and switching between flux chambers as well as acquiring emission data from the gas analyzer, standard gases and other associated equipment.

To assess odor intensity before and after the application of SOP Lagoon, an odor panel test was conducted. A Nasal Ranger®Field Olfactometer (St. Croix Sensory, Inc., Stillwater, MN, USA) was used by four trained panelists to assess odor intensity from the samples (Figure 3). The Nasal Ranger uses a "dilution to threshold" ratio by mixing odorous air with carbon filtered air at different dilutions

to determine the dilution of odor that is not detectable by the panelist. The dilution to threshold ratio is a measurement of the dilution, using filtered odor-free air, needed for the odor from the air under the flux chamber to be perceived by 50% of the panel members [25]. Each odor panelist analyzed each sample four times to develop an average. The odor assessments were conducted on days 1, 3 and 7 of each week to determine odor intensity over the tests period.

Figure 3. Measurement of odor intensity using the Nasal Ranger approach.

2.5. Emission Calculation

The measured gas concentrations in the flux chambers over the 20-min period were truncated to remove the first 7 and last 2 min of each sample period to prevent any possible carry-over effects. The total flux of each gas (mg/h) was then calculated using the following equation:

$$\text{Total flux} \left(\frac{\text{mg}}{\text{hr}} \right) = \frac{\text{MIX} \times \text{FL} \times 60}{MV} \times MW \times Conv$$

where MIX is the net concentration that is equal to the gas concentration in the air being sampled minus the background concentration in the fresh inlet air in either ppm or ppb, FL is the ambient air flow rate at 8 L/min, 60 is the conversion from minute to hour, MW is the molecular weight of the gas in grams per mole, Conv is a conversion factor of 10^{-3} for the concentration in ppm and 10^{-6} for the concentration in ppb and MV is the volume of one molar gas at temperature 20 °C (24.04 L/mole).

The surface-emission rate (mg/h/m^2) of the sample in each barrel was calculated using the following equation:

$$Surface\ Emission\ Rate = \frac{Total\ Flux}{Surface\ Area}$$

where the surface area is the cross-section area of the 208 L (55-gallons) steel drum barrel directly under the flux chambers, approximately 0.25 m^2. The emission rate per each cubic meter of manure was calculated based on the surface emission rate, the surface area of the barrel and the amount of manure in each barrel (65 L).

The average reduction in emissions (%) after applying the HIGH dose was calculated using the following equation:

$$Average\ reduction\ in\ emissions = \left(\frac{Total\ emissions\ from\ CONT - Total\ emissions\ from\ HIGH}{Total\ emissions\ from\ CONT}\right) \times 100$$

where the total emissions from CONT and HIGH were calculated as the summation of the average daily emissions over the experimental time for both experimental rounds.

2.6. Odor Intensity Calculation

The data recorded by the odor assessors were used to calculate the geometric average dilution-to-threshold (ADT) as follows [26]:

$$ADT_n = 10^{\frac{\log(DT)_n + \log(DT)_{n+1}}{2}}$$

where *n* is the device setting number reported by an assessor for a reading, $(D/T)_n$ is the unit dilution to threshold and $(D/T)_{n+1}$ is the next higher unit dilution to threshold.

2.7. Statistical Analysis

The average daily emission rates from the different lagoon samples were compared to evaluate their respective impact. The data were analyzed using a three-way ANOVA to determine the effect of three factors (experimental rounds (two rounds), SOP treatments (HIGH, LOW and CONT) and treatment time (seven days)) and their interactions. Differences were declared significant at $p \leq 0.05$ and showed a trend at $0.1 \leq p < 0.05$. All means are presented as least squares means (LSM) and were determined using the LSM package in R [27]. Pairwise comparisons of the treatments LSM were determined using the Tukey procedure. The CLD function in the multcompView package in R was used to visualize the pair comparison of the treatment groups [28].

3. Results and Discussion

3.1. Effect of SOP on GHG Emissions

The GHG emission rates over the experimental time are shown in Figure 4. Methane and carbon dioxide are products of the anaerobic degradation of the organic matter in manure. Carbon dioxide can also be produced via the aerobic microorganisms and the oxidation of CH_4 when enough oxygen is present in the surface layers of the manure [29]. Nitrous oxide is produced through the nitrification and denitrification processes [30,31]. Sommer et al. mentioned that although methane is produced strictly under anaerobic conditions, oxygenation via nitrification of NH_4^+ to nitrate (NO_3^-) is necessary for N_2O production [32].

Figure 4 shows CH_4 and CO_2 emission rates that were pronouncedly fluctuating along with ambient moisture; higher emission rates were measured during periods with higher moisture (i.e., during the night time). The fluctuation of the N_2O emission rates was less pronounced than the other two gases in the first experimental round. The manure treated with SOP Lagoon versus CONT had lower emission rates of CH_4, CO_2 and N_2O. Using the average CH_4 emission rates from both experimental rounds, the maximum emission rates of 24.9, 33.6 and 33.0 mg/h/m^2 were determined after 130, 154 and 130 h from the experiment start time for the HIGH, LOW and CONT, respectively. Similarly, maximum emission rates of CO_2 of 0.96, 1.17 and 1.1 mg/h/m^2, were determined after 37.3, 11.7 and 11.7 h from

the experiment start time for the HIGH, LOW and CONT, respectively. Maximum emission rates of N_2O of 0.30, 1.13 and 0.66 mg/h/m^2 were determined after 165.7, 51.3 and 51.3 h from the experiment start time, respectively. The reason for the spike in N_2O at around 220 h was unable to be assigned.
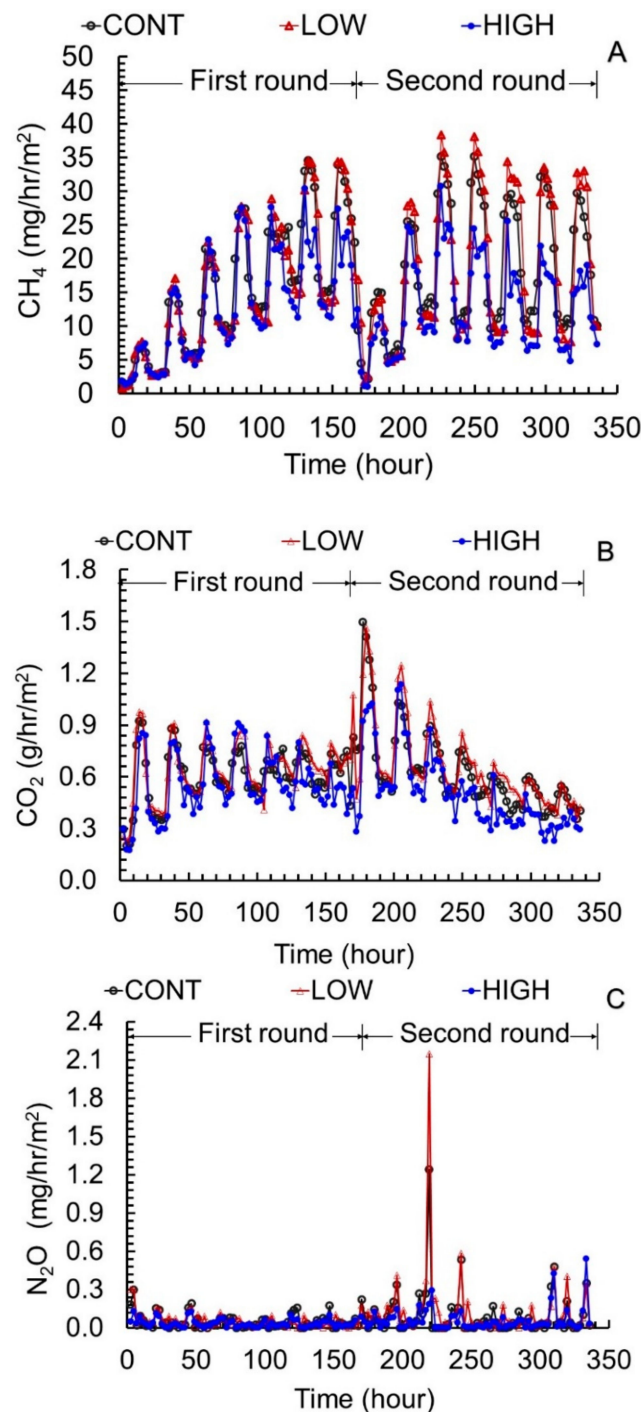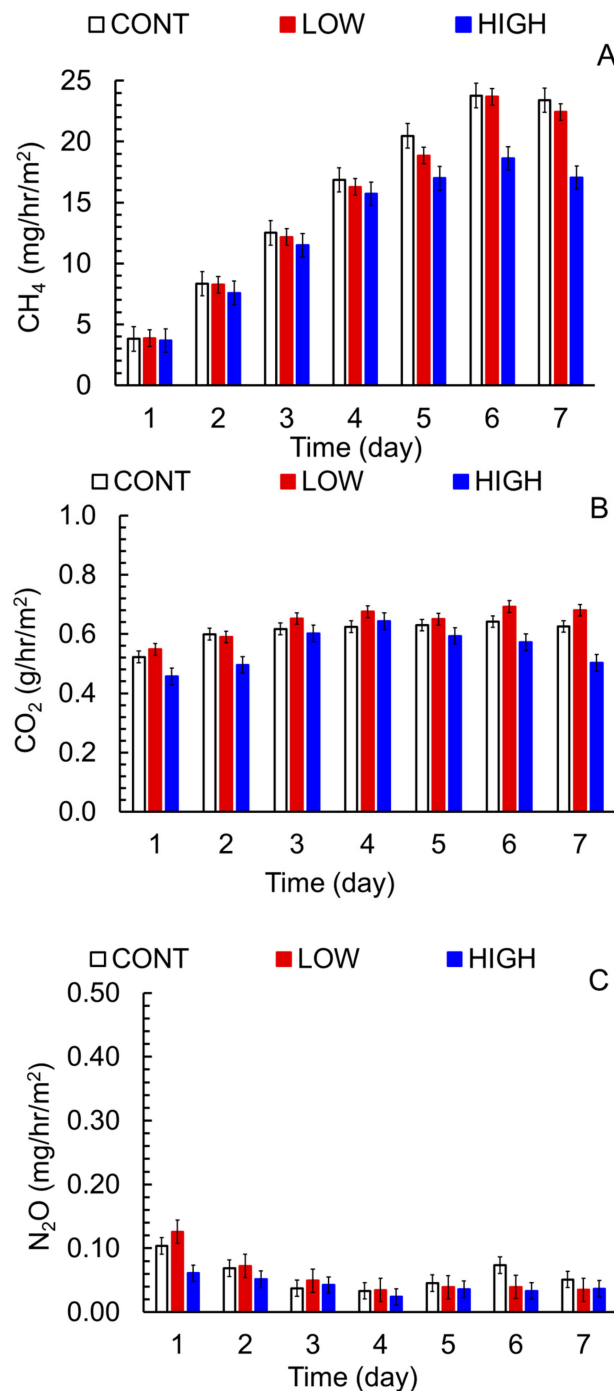

Figure 4. Continuous emission rates of greenhouse gas (GHG) over the experimental time: (**A**) methane, (**B**) carbon dioxide and (**C**) nitrous oxide.

The average GHG emission rates for each day during the first and second experimental rounds are shown in Figures 5 and 6. The average CH_4 emission rates during the first experimental round increased with the increase of storage time across all treatments. During the second experimental round, the average emission rates of CH_4 increased until the third day, then decreased for all groups, with a more pronounced decrease for HIGH. The increase of CH_4 emissions with the increase in storage

time is in accordance with the literature. Sommer et al. mentioned that the progressive dynamics of methane emissions may suggest microbial succession or the use of different pools of organic matter in the slurry [32]. The authors also indicated that fresh slurry had lower CH_4 emissions at the early stages of manure storage (ca. 10 days) due to a microbial lag phase, unless the slurry was inoculated with fermented slurry. In the present experiments, the manure was collected from the lagoon which likely assured the presence of methanogens that needed a few days to be established. This is in contrast to what was reported by Borgonovo et al., who showed peak emissions at day 4 [24]. These observed differences between the experiments may be due to the substrate to which the treatment was applied. In the present study, liquid manure was used versus fresh slurry in the Borgonovo et al. study.

Figure 5. Average daily emission rates of GHG over the experimental time in the first round: (**A**) methane, (**B**) carbon dioxide and (**C**) nitrous oxide. Y error bars are standard errors.
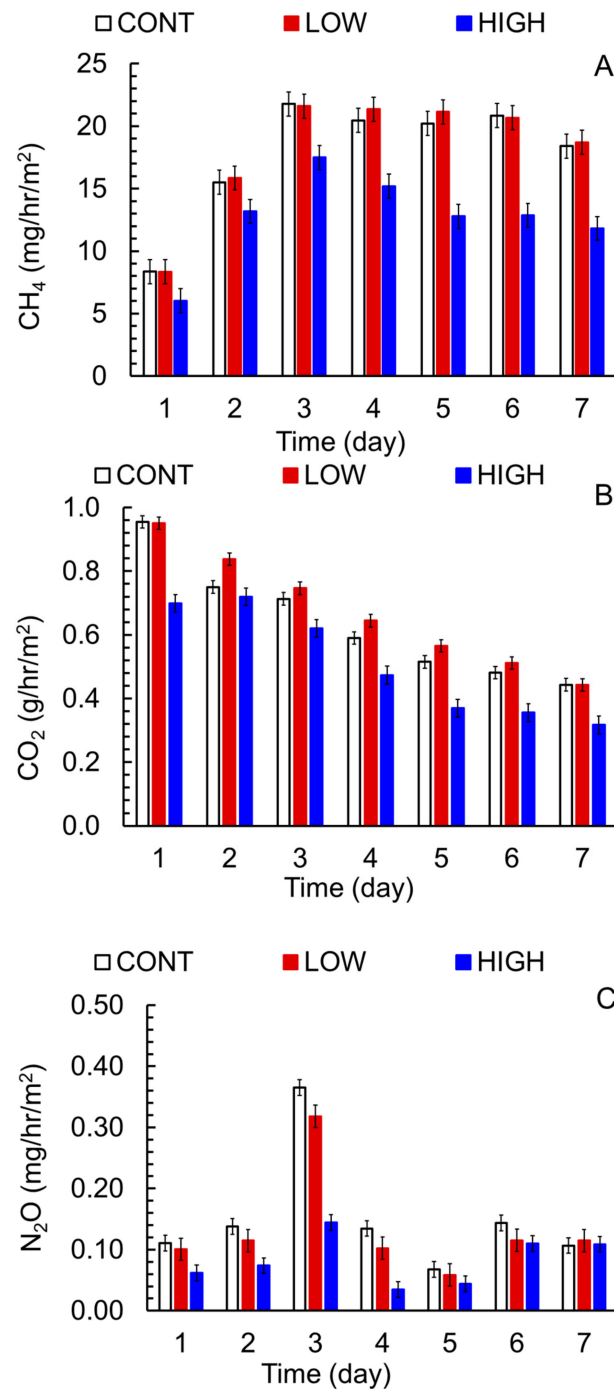
Figure 6. Average daily emission rates of GHG over the experimental time in the second round: (**A**) methane, (**B**) carbon dioxide and (**C**) nitrous oxide. Y error bars are standard errors.

For each day in both experimental rounds, the HIGH dose achieved greater GHG emission reductions compared to LOW. Table 1 shows the statistical analysis results of the effects of SOP Lagoon treatment, storage time, experimental round and interaction of storage time and experimental round on gas emission rates of CH_4. The emission rates of CH_4 from the manure treated with the HIGH dosage were significantly different from that of the CONT and LOW. There were no significant differences in the emission rates of CH_4 from the CONT versus LOW treatments.

Table 1. Least squares means (LSM) and mean standard errors (SEM) of the overall gaseous emissions for "SOP Lagoon" applied at LOW and HIGH rates vs the untreated CONT lagoon water across all four replicate weeks.

Trait	LSM of SOP Lagoon Treatments			SEM	*p*-Value						
	CONT	LOW	HIGH		*Treatments(Trt)*	*Days*	*Rounds*	*Trt × Days*	*Trt × Rounds*	*Days × Rounds*	*Trt × Days × Rounds*
CH_4 (mg/h/m^2)	16.76 [a,*]	16.65 [a]	12.89 [b]	0.68	<0.001	<0.001	0.031	0.90	0.19	<0.001	1.00
CO_2 (g/h/m^2)	0.62 [a]	0.66 [a]	0.53 [b]	0.02	<0.001	<0.001	0.857	1.00	0.33	<0.001	1.00
N_2O (mg/h/m^2)	0.11 [a]	0.10 [a]	0.06 [a]	0.01	0.051	0.006	<0.001	0.97	0.35	0.002	0.92
NH_3 (mg/h/m^2)	15.82 [a]	14.61 [a]	8.58 [b]	0.55	<0.001	0.003	0.045	0.98	0.29	<0.001	0.96
Odor (D/T)	53.17 [a]	56.36 [b]	48.51 [c]	0.89	<0.001	<0.001	<0.001	<0.001	0.10	<0.001	0.15

* Least-squares means with a different letter in each column are significantly different at the *p* = 0.05 level. [a, b, c] Means with different superscripts differ at *p* < 0.05.

The average emission rates of CO_2 during the first experimental round for all the treatments increased until the fourth day, then slightly decreased for the HIGH and remained almost constant until the end of the storage time for the CONT and the LOW (Figure 5). In the second experimental round, the CO_2 emissions decreased with the increase of storage time for all treatments (Figure 6). The statistical analysis showed significant effects ($p < 0.05$) of the SOP Lagoon treatment, storage time and the interaction of the storage time and the experimental round on the emissions of CO_2. The emission rates of CO_2 from the manure treated with HIGH were lower than those from CONT and LOW. The CO_2 emissions between the CONT and LOW treatments were similar. The differences in the emission rates of CO_2 between both experimental rounds might be attributed to the characteristics of the manure and the biochemical processes occurring during storage. Møller et al. mentioned that even after the establishment of methanogens, aerobic degradation may also still occur at the manure–air interface where oxygen can exchange with the manure [29].

The average emission rates of N_2O during the first round of the experiments decreased after the first two days and remained relatively constant until the end of the storage time. During the second experimental round, the emission rates of N_2O were relatively higher than those determined in the first experimental round. The statistical analysis showed significant effects ($p < 0.05$) of SOP Lagoon on the average emission rates as a function of storage time, experimental round and the interaction between the experimental round and time. The main effect of treatment alone was not significant but did show a trend for N_2O emissions ($p = 0.051$).

Compared to the CONT, the HIGH treatment achieved average emission reductions of 22.7% and 14.7% for CH_4 and CO_2, respectively ($p < 0.05$). The HIGH vs CONT treatment also showed an emission reduction of 45.4% for N_2O.

3.2. Effect of SOP on NH_3 Emissions

The emission rates of ammonia over the storage time are shown in Figure 7. Similar to the GHG emissions, the ammonia emissions from all the treatments also had a diurnal pattern: higher emission rates were determined at higher ambient temperatures. During the measurement of ammonia emissions from dairy manure storage, Grant and Boehm found a rapid increase in the NH_3 emission rates with an increase in ambient air temperature [33].
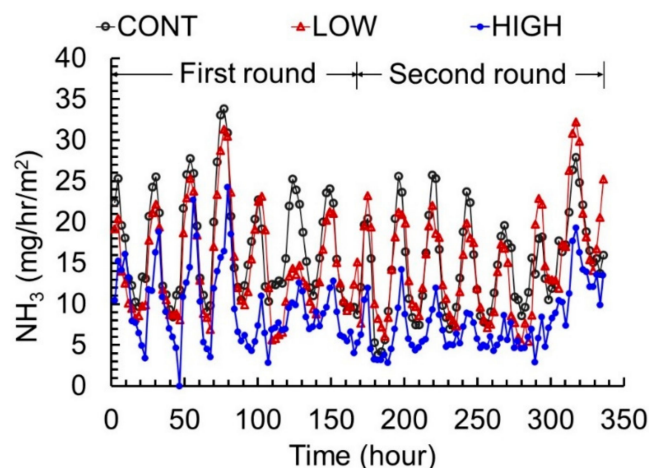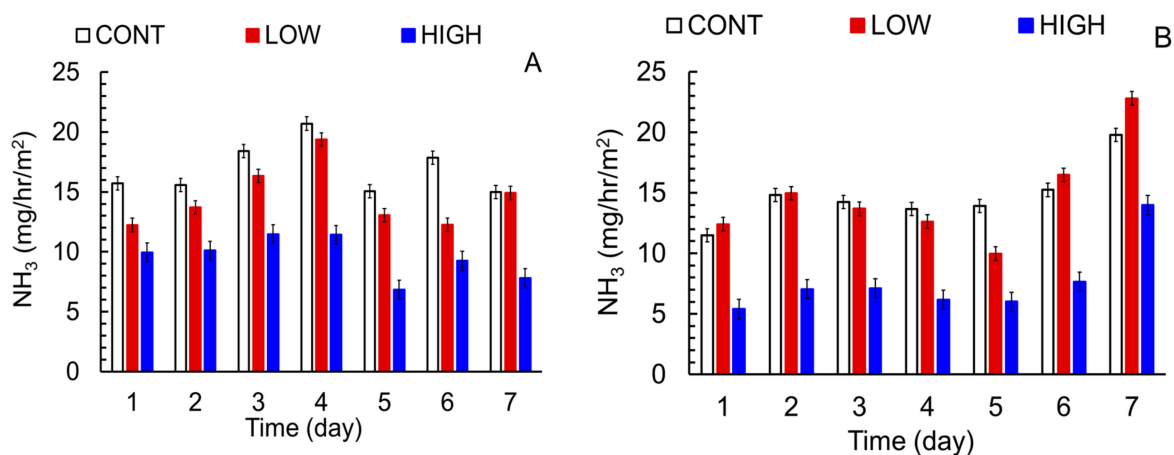

Figure 7. Continuous emission rates of ammonia over the experimental time.

The daily average emission rates of NH_3 over the storage time for both experimental rounds are shown in Figure 8. The average emission rates in the first experimental round increased during the first four days, then decreased. During the second experimental round, the emission rates of NH_3 increased after the fourth day of storage. The maximum average emission rates of ammonia, over the two experimental rounds, were 16.0, 26.8 and 28.4 mg/h/m^2, which were determined after 79.3,

149.3 and 74.7 h from the start of experiments for HIGH, LOW and CONT, respectively. Table 1 shows the results of the statistical analysis of the effect of SOP Lagoon treatment, storage time, experimental round and interaction of storage time and experimental round on the emission rates of NH_3. The emission rates of NH_3 from the manure treated with HIGH were lower ($p < 0.05$) than those of CONT and LOW. Emission rates of NH_3 for LOW and CONT were similar. Compared with CONT, applying a HIGH dose of SOP Lagoon achieved a 45.9% reduction in ammonia emissions.

Figure 8. Average daily emission rates of ammonia over the experimental time: (**A**), first round; and (**B**), second round. Y error bars are standard errors.

3.3. Effect of SOP on Odor

Odor intensity after the application of SOP Lagoon was quantified using the dilution to threshold (D/T) ratio used to describe how strong an odor is perceived by four blinded odor panelists, with higher numbers showing stronger odors. Figure 9 shows the average of all data collected from all four panelists during the two experimental rounds for each treatment on day 1, 3 and 7. Relatively lower values ($p < 0.05$) of the geometric mean of D/T were determined from the manure treated with HIGH versus CONT and LOW. The LOW treatment was shown to be significantly higher than the other two treatments ($p < 0.05$). Table 1 shows the effects of the SOP treatments, storage time, experimental rounds, the interaction of storage time and treatments and the interaction of storage time and experimental rounds on the geometric mean of D/T.
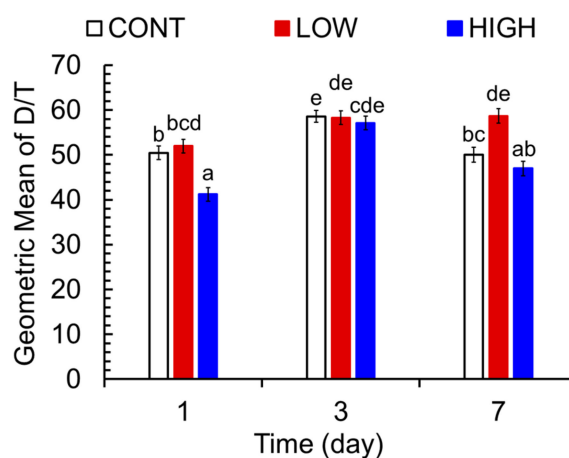
Figure 9. Average geometric mean of odor dilution to threshold (D/T) over the experimental time. Y error bars are standard errors. Different letters show significant differences at the 0.05 level.

4. Discussion

The average emissions (per each m^3) of different gases were calculated by averaging the emissions from both experimental rounds (Table 2). It was assumed that the characteristics of lagoon water did not change over the short duration of the trial. Although manure characteristics were not determined in these experiments, the data presented in Table 2 could be applied to determine the potential reduction of different gaseous emissions from a certain lagoon volume after applying the SOP additive. For example, applying the high dose of SOP for a lagoon with a volume of 34,069 m^3 could reduce the emissions of CH_4 and NH_3 by approximately 86 and 160 kg per week. It should be mentioned that this lagoon volume was calculated to hold the flushed manure (0.378 m^3/cow/day) for 90 days [34].

Table 2. Average emissions from untreated and treated lagoon water (mg/m^3/h) *.

Emitted Gas	SOP Lagoon Treatments		
	CONT	LOW	HIGH
CH_4	64.66 ± 10.70	64.24 ± 8.52	49.71 ± 10.05
CO_2	2399.24 ± 381.45	2530.96 ± 222.55	2044.27 ± 288.90
N_2O	0.41 ± 0.23	0.37 ± 0.25	0.24 ± 0.09
NH_3	61.01 ± 10.93	56.36 ± 9.56	33.08 ± 5.05

* The data is the average of the four replicates over the two experimental rounds.

A variety of additives have been applied to reduce emissions from manure. Although the composition and mechanism of the emission reduction of several additives are known, information on many other commercial additives is not available because of confidentiality and limits in the marketing literature [13].

Calcium sulfate (gypsum) can be found abundantly in nature and has been used to improve soil properties. Flue gas desulfurization gypsum is a by-product of scrubbing sulfur from combustion gases at coal-fired power plants [35]. The application of flue gas desulfurization gypsum in agriculture has shown positive environmental impacts [35]. Different forms of gypsum have been tested for the mitigation of GHG and ammonia emissions from livestock effluents. The results have had varying results: while some studies reported a decrease in ammonia emissions after the addition of gypsum, not all have demonstrated the efficacy of gypsum in reducing the release of GHGs. Many of the results were obtained using a considerable amount of material (3% to 10% of manure wet weight) making the application not practical in real-world conditions. Borgonovo et al. first published results on this specific commercial additive (SOP LAGOON), made of gypsum processed with proprietary technology, and found that the addition of the products to fresh liquid manure has a reduction potential of 21.5% of CH_4, 22.9% of CO_2, 100% of N_2O and 100% of NH_3 emissions on day 4, even at very low dosages [24]. It should be mentioned that similar to other commercial additives, the exact manufacturing process of SOP Lagoon is unknown due to confidentiality [13]. This may limit the complete understanding of the mechanism of SOP Lagoon on emission reduction. The shorter duration of application is consistent with Borgonovo et al. but this time frame may be too short to fully understand the long term effects of emissions on a commercial dairy lagoon after application of SOP LAGOON [24].

The amount of product used, even at the HIGH dose, is not sufficient to justify a purely chemical reaction that would reduce the gaseous emissions, suggesting some other mechanisms of action. Other SOP products have been used by several researchers for other applications. SOP SQC 233, for example, was found to decrease the total amount of pathogens for a variety of pathogen types in cow bedding [36–38] and synthetic rubber mat covered pens [39] as well as a decrease in the somatic cell count (SCC) in milk, especially for primiparous cows [37,40–42]. Bronzo et al. and Lynn Sharkey et al. found that treating manure with SOP could decrease the pathogen load of manure [43,44]. These studies seem to indicate that the applied HIGH dose of SOP Lagoon might decrease the number of methanogens that produce methane during the storage of manure as well as hydrolytic microorganisms

and their excreted enzymes that biodegrade organic nitrogen into ammonium. Further studies could investigate the mechanism of emission reduction using SOP Lagoon.

Future research is still needed to investigate the relationship between the microbial communities in the liquid manure and the emission reduction using SOP Lagoon. These studies could be extended to longer periods on a larger scale and include the addition of new effluent to be more representative of typical storage conditions. In addition, the mechanism of emission reduction could be investigated.

5. Conclusions

Applying SOP Lagoon to liquid manure at a dose of 61.6 g per m^3 of manure significantly reduced emissions of carbon dioxide, methane, ammonia and nitrous oxide. The same dose of SOP also significantly reduced odor intensity. Future research is needed to investigate the mechanism of SOP for emission reduction and its relationship with the microbial communities in the liquid manure. More studies are needed to study long term effects of this additive, as well as the addition of effluent throughout the study, should be completed. Large scale application of this additive should also be studied to better understand the direct impacts on real-world dairy systems. In addition, the effects of this additive after land application of lagoon water has yet to be elucidated.

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