SLURRY COVER: CAN IT HELP REDUCING GHG EMISSION FROM SLURRY SURFACE IN MALAYSIA

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ABSTRACT. Liquid manures stored produce a significant amount of methane (CH4) and ammonia (NH3) gas from biological anaerobic fermentation. Studies carried out to evaluate a potential biological cover on inhibiting gases emission and simple cover design to overcome the high cost of biogas production on covered lagoon types that are available on the market. The agriculture waste from rice straw, cocopeat, hay, and sawdust were used as biological covers in reducing CH4 emission and NH3 volatilisation from ruminant slurries. During ninety days of the undisturbed storage period, immediate reduction of CH4 and NH3 gases fluxes were observed after the application. Rice straw and coco peat were found to effectively reduce the emission of CH4 and NH3 between 45.5% and 56.9%. Other biological cover showed a slightly lower reduction on NH3 volatilisation and much lower in CH4 inhibition percentage (28-29%). Covering method was found to be suitable with Malaysia's climate in reducing greenhouse gas emission from slurry manure.

Keywords: methane mitigation, ammonia volatilisation, slurry, bio-cover, biogas

INTRODUCTION

Proper manure management is important as manure storage contributes to the release of greenhouse gas (GHG) emission up to 18% of the total agriculture emission (Pattey *et al*., 2005; Chadwick *et al*., 2011; Sommer *et al*., 2013). Greenhouse gas emission especially methane (CH_4) during slurry manure storage is significant, but strategies are being explored and implemented to reduce these emissions. To date, Malaysia's manures contribute to 1.714 Gg yr^{-1} CO_2 eq. GHG emission (Ministry of Natural Resources and Environment, 2018). One of the ways to reduce this emission is by having biogas from bio-digester which generates renewable energy. However, this technology is limited in application, as it requires large capital, high maintenance cost, and a large number of animals to make the system economically viable and productive. Therefore, there is a need for alternative approaches to reduce CH_4 and other GHG emissions from slurry storage facilities especially for small-medium livestock farmers in Malaysia. Current typical dairy and some beef manure management in most developed countries are illustrated in Figure 1 (Bastami, 2016). During manure storage, slurry storage acts as point sources, greenhouse gas emissions may be contained through improved storage conditions, and permeable surface coverings (natural crusts and artificial covers) are increasingly recognized for their ability to reduce various gaseous emissions including ammonia (NH_3) (Berg *et al*., 2006). Surface cover using agricultural waste not only act as a physical barrier but to retain gaseous emission (CH_4 and NH_3) (Guarino *et al*., 2006). It is a medium for microbes to oxidize methane and as an excellent medium for a nitrification-denitrification process (Portejoie *et al*., 2003; Guarino *et al*., 2006; Petersen and Ambus, 2006; Hansen *et al*., 2009). The biological cover typically contains fibrous material and later hardens following prolonged undisturbed storage, namely known as the crust.

The slurry crust is defined as a fibrous layer on the slurry surface, which develops during the slurry storage (Pain and Menzi, 2011). Slurry crusts are formed due to solids in the slurry being carried to the slurry surface by gas bubbles produced by microbes during microbial degradation of the organic matter (Misselbrook *et al*., 2005). Crusts that are formed on cattle slurry by natural processes can be promoted by adding chopped straws or fibrous materials (Sommer and Husted, 1995; Pain and Menzi, 2011; Aguerre *et al*., 2012). The presence of crust on the slurry surface may be colonized by methane-oxidizing microbes (Duan, 2012; Duan *et al*., 2013). This oxidation by slurry crusts offers a potentially important sink for the CH_4 generated by methanogen in liquid slurry beneath it but may increase the N_2O emission due to nitrification of NH_4^+ and subsequent denitrification of NO_3^- in the crust microenvironment (Hansen *et al*., 2009).

Methane gas is a potent gas produced by methanogen in oxygen-deficient environments and has global warming potentials on a 100-year time horizon that is 34 times greater than carbon dioxide (Myhre *et al*., 2013). In Malaysia, the awareness for CH_4 emission from slurry is little because it may not have any short-term effects on the local environment, animals, and farmers, hence there is no direct consequences for the farm's economy. Meanwhile, NH_3 volatilisation is a transfer of N from animal manure to the atmosphere. They represent a loss of valuable fertiliser N content from manure. In addition, an anthropogenic NH_3 emission to the troposphere indirectly causes environmental damage such as soil acidification and eutrophication on watercourse (Portejoie *et al*., 2003; Petersen *et al*., 2012). Earlier studies showed a significant reduction of up to 80% in NH_3 emissions from stored slurry with natural crusts or floating covers (Portejoie *et al*., 2003; Misselbrook *et al*., 2005).

Addition of a substrate as slurry cover is considered an additional cost. Thus, recycling agricultural by-products is a way of reducing farmer costs conveniently. The objective of this study is to provide an initial evaluation of the biological cover to mitigate emission from the

Figure 1. Greenhouse gas emission from common slurry management in dairy and beef farms in developed countries (Bastami, 2016).

stored slurry. It is hypothesized that biological cover creates a physical barrier, promotes crust formation which helps to reduce CH_4 emission and NH_3 volatilisation from the slurry surface. This approach is considered as a simple trap suit to most small-medium dairy farmers.

MATERIALS AND METHODS

Slurry biological cover

Cattle slurry origin and characterization

Fresh cattle slurry (FS) from Brakhmas cows breed was obtained from a reception pit at MARDI Kluang Research Station, Kluang, Johor. The cattle are of the average 3 years of age and at first parity stage, weighed around 250-300 kg. These animals were fed with total mixed ration (TMR) at a 3% dry matter basis of bodyweight, which comprises 60% concentrates and 40% fresh grass (% dry matter basis). The concentrates contents are mainly palm kernel expeller (PKE), ground corn, soya bean meal, soya bean hull, ground rice hull, crude palm oil (CPO), molasses, and limestone with the addition of less than 0.002% minerals and trace elements for the animal growth requirement. The 500 kg slurry obtained was sieved to pass a 2.5 cm mesh to remove large particles of uneaten straw and hay which was kept in a 700 L plastic container and stored undercover for 24-48 hr prior to use. The slurry physicochemical compositions (pH; dry matter, DM; volatile solid, VS; carbon and nitrogen ratio) were characterised before the experimental design was carried out. Initial slurry characteristics were 9.0 ± 01.8% dry matter (DM), 70.2 ± 0.4% volatile solids (VS), total percentage % carbon (C) 14.5 ± 0.31, total percentage % nitrogen (N) 4.07 ± 0.06, C:N ratio 3.5:1, and pH 6.84 ± 0.23.

Cattle slurry was transferred into 30 L *high-density polyethylene* (HDPE) plastic drums (31.2 cm diameter x 52.0 cm height), such that each drum contained a final weight of 20 kg with and without agriculture by-products as biological cover. The biological cover was added on the slurry surface without any disturbance at about 1-1.5-inch thickness (Figure 2). There were 4 types of agriculture by-products used which were known as: i) slurry + hay (Hay), ii) slurry + sawdust (Sawdust), iii) slurry + rice straw (Straw), and iv) slurry + cocopeat (Cocopeat). The experiment was carried out for 90 days, between October 2017 till January 2018.

Figure 2. Biological cover application on the slurry surface.

Slurry dry matter (DM) and volatile solids (VS) content

Slurry dry matter (DM) and volatile solids (VS) were determined by drying 10 g slurry samples at 80-105°C to constant weight (16 hr) and a loss on ignition at 450°C for 16 hr in muffle furnace Carbolite CWF 1200 (Carbolite Ltd, UK).

Total carbon (C) and nitrogen (N)

The total C and N of fresh slurry were measured by Elemental Analyzer-4 by Estate Research & Advisory Services, Kajang Selangor

Slurry pH

Slurry pH and crust were measured using a Hanna pH electrode probe (model HI 991003; Hanna Instrument, USA).

Greenhouse gases measurement

Greenhouse gas fluxes were sampled from the *ca.* 10-15 litres vessel headspace through a butyl rubber septum. Headspace gas samples were taken immediately (T0) securing the lid in place, after 30 (T30) and 60 minutes (T60). Gas samples were placed in 20 mL pre-evacuated gas vials and analysed by using Agilent 7890B gas chromatogram (GC). The GC was equipped with Hayesep Q, 8ft x1/8in x2.0mm columns, and equipped with a thermal capture detector (TCD). Gas fluxes were calculated based on the linear increase in gas concentration between the T0 and T60 samples for an hour, headspace volume, and slurry weight. Cumulative gas emissions for the storage period were calculated by interpolating the measurements between adjacent sampling points using the trapezoidal rule (Cardenas *et al.*, 2010).

Relative ammonia volatilisation

Measurement was carried out during a closed system concurrent with the gas sampling period. Relative NH_3 volatilisation was determined using a 0.02 M orthophosphoric acid (H_3PO_4) trap placed in a non-ventilated (sealed) environment (Misselbrook and Powell, 2005). The acid trap was carefully suspended inside this headspace, from the lip of the vessel. Following the one-hour 'incubation' when the lid remained in place, the traps were removed and the ammonium-N (NH_4-N) concentration in the H_3PO_4 acid was determined as described by Mulvaney (1996). Prior to incubation at 30°C, 15 µL of 6% Na_2EDTA, 60 µL of Na-Salicylate-nitroprusside and 30 µL of hypochlorite solutions were added. Na-Salicylate-nitroprusside solution consisted of 7.8% ($^w/_v$) Na-Salicylate and 0.125% ($^w/_v$) Na-nitroprusside, while hypochlorite solution (pH 13) contained 2.96% ($^w/_v$) NaOH, 9.96% K_2HPO_4 ($^w/_v$) and 10% ($^v/_v$) Na-hypochlorite. Absorbance readings were measured after 30 min incubation using a microplate reader Biotek PowerWave XS at wavelength 667nm and analysed by Gen 5 software Biotech (Instruments, Inc., USA).

RESULTS

Slurry biological cover

The addition of biological cover did not change slurry characteristics (Table 1 and Table 2) although the DM content was found lower at the end of the experiment. The use of biological cover showed a significant reduction in NH_3 volatilisation compared to Ctrl (Figure 4a, b). Biological cover acts as a physical barrier and such volatilisation are retarded during the entire storage period. Even at day 90, NH_3 losses were significantly high with inhibition between 28.5% and 39.6% compared to day 0 with an average inhibition of 85.8%. Continuous inhibitions resulted in cumulative NH_3 volatilisation which were 45.5% and 55.6% lower compared to Ctrl. The lowest NH_3 emission was when using Cocopeat cover at 68.49 mg m^{-2} compared to Ctrl at 154.4 mg m^{-2}.

The use of biological waste as a physical barrier is able to inhibit GHG loses mainly CH_4. All substrates used except Straw immediately (Day 0) blocked CH_4 fluxes to the atmosphere after covers were applied (Figure 5a, b). However, CH_4 fluxes from Straw showed significant inhibition between 25 to 80% the next day (Day 1) until the end of observation. The total emission from Straw was 55.4% (11.5 g Kg^{-1} Vs) which was lower than Ctrl (25.7 g Kg^{-1} Vs). Cocopeat as biological cover represents the highest inhibition of 56.9% (11.1 g Kg^{-1} Vs).

Table 1. Slurry characteristics during storage observation.

Treatment	Start				End			
	%DM (±SEM)		% VS (±SEM)		%DM (±SEM)		% VS (±SEM)	
Hay	10.5	±2.00	70.6	±1.10	7.4	±0.09	72.4	±0.36
Cocopeat	11.8	±0.95	70.9	±0.64	7.4	±0.05	71.9	±0.07
Straw	10.2	±1.83	69.8	±0.60	6.5	±0.16	72.2	±0.14
Sawdust	8.1	±0.81	70.1	±0.55	8.4	±0.18	75.0	±1.86
Ctrl	9.0	±1.80	70.2	±0.35	6.9	±0.15	70.5	±0.20

Table 2. The effect of biological cover on slurry pH and crust pH.
* Crust pH was measured at the end of the experiment

Substrate	Slurry pH				Crust pH (bio-cover) (±SEM)*	
	Initial (±SEM)		End (±SEM)			
Hay	7.05	±0.007	7.00	±0.005	7.34	±0.090
Cocopeat	7.05	±0.003	7.01	±0.029	6.75	±0.100
Straw	7.05	±0.005	6.99	±0.023	7.25	±0.034
Sawdust	7.03	±0.017	6.99	±0.013	7.17	±0.105
Ctrl	7.07	±0.007	7.02	±0.018	-	-

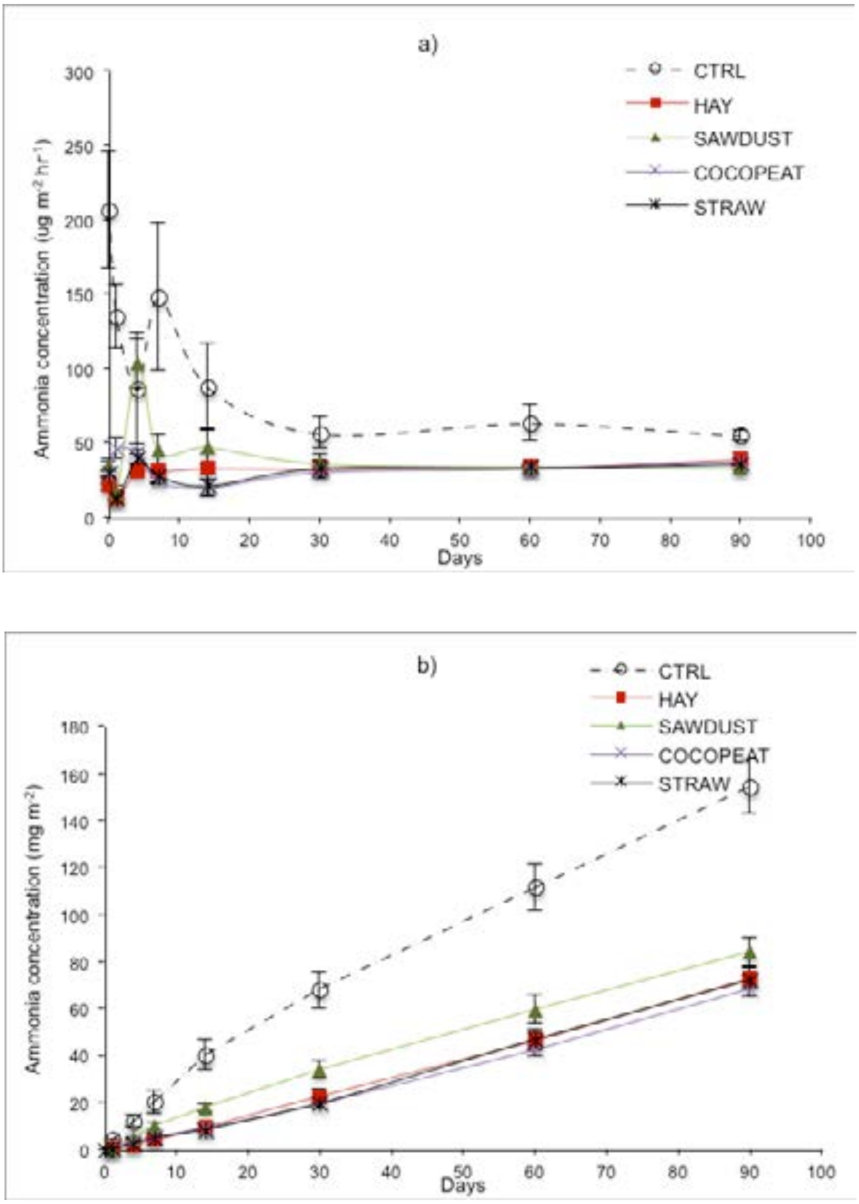

Figure 4. Ammonia fluxes (a) and cumulative emission (b) of slurry storage with biological cover.

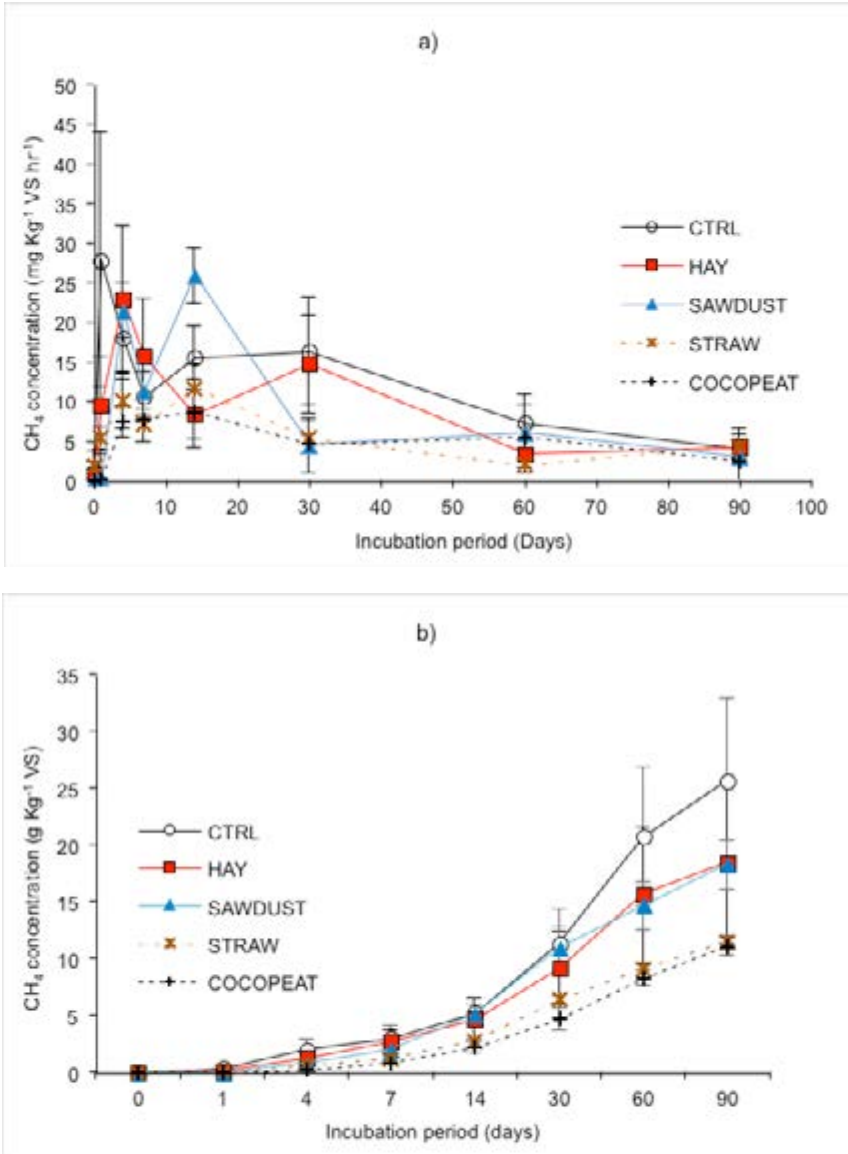

Figure 5. Methane fluxes (a) and cumulative emission (b) of slurry storage with biological cover.

DISCUSSION

Slurry biological cover as a physical barrier

Recycling agri-waste to promote crust formation on the slurry surface is one of the ways to reduce CH_4 loss. In this study, the crust formed as a thin layer and not well hardened as typical crust as in anaerobic lagoon that has been observed in the UK (Bastami *et al.*, 2016a). Therefore, there is a possibility less or zero potential of methane-oxidizing bacteria (MOB) and ammonia-oxidizing bacteria (AOB) to dominate the crust that utilized CH_4 and NH_3 emission (Petersen and Ambus, 2006; Hansen *et al.*, 2009; Duan, 2012; Nielsen *et al.*, 2013). These microbes are responsible for reducing these gases from being emitted to the air biologically or naturally.

The uses of biological cover on the slurry surface did not trigger physiochemical changes on the slurries and no other metabolism could trigger self-acidification in this study (Bastami *et al.*, 2016b; Bastami *et al.*, 2020). This indicates that the slurries undergo a typical process of fermentation and decomposition on equatorial climate. Any large changes in slurry pH and temperature will retard these processes and may reflect on GHG emissions. The slurry covers were also at neutral conditions following the emulsion underneath. The lower DM content at the end of the experiment was due to the decomposition and sedimentation of organic matter at the bottom of the drums.

The use of agri-waste benefits the bio-cover in bad odours absorption (English and Fleming, 2006). Bio-cover did enhance the aerobic condition in the lagoon surface and biologically retarded the odorants (Zhang *et al.*, 2013). In this study, it showed a positive sign in reducing NH_3 and CH_4 emission similar to other studies (Hansen *et al.*, 2009; Matulaitis *et al.*, 2015). An NH_3 fluxes inhibition in this study was similar if slurry was covered using Leca balls (Balsari *et al.,* 2006). In addition, possible higher inhibition from cover can be obtained if the crust pH formed is lower than pH 7 similar to the result on Cocopeat. This lower NH_3 emission may be associated with lower crust pH that retains in the solubilized form (NH_4^+) from volatilisation similar to Berg *et al.* (2006) and Guarino et al. (2006). The crust formed with lower pH value than neutral is a significant approach to inhibit greenhouse gas emission including NH_3 (Berg *et al.*, 2006; Guarino *et al.*, 2006; Smith *et al.*, 2007; Hansen *et al.*, 2009).

The result of this study on CH_4 emission by the uses of slurry covers represents a possible new practice to farmers in Malaysian tropical environment although some other studies were controversial, e.g., Berg *et al.* (2006) which reported increased GHG emission. This contradiction is probably due to the psychrophiles condition (temperature below 20°C) in the previous study and dominated by different methanogen groups (Mah and Smith, 1981). Similarly, in this study, the reduction of CH_4 emission was slightly lower than a study by Matulaitis *et al.* (2015) using pig slurry and at lower environment temperature. It emits more CH_4 when applied at 25°C, and similar to Berg *et al.* (2006) and Misselbrook *et al.* (2016) which reported that usage of clay granules as covers did not give any impact on CH_4, but reduced NH_3 by 77%.

Adding biological cover on the slurry surface may not be favourable by the farmers as this affects business cost and profit margin. In addition, biological cover shall remain on the slurry surface until the next emptying process where emptying frequency may reflect on the amount and cost of the biological cover besides the number and size of the waste pond used. Therefore, a farmer may utilise agri-waste products such as straw, hay, and sawdust from the surrounding area. Furthermore, compared to physical and chemical methods, this biological method is more feasible and economical. This is important for the typical small-medium size farmers in Malaysia.

Other biocover as biogas trap

Other cover approaches such as covered anaerobic lagoon or biodigester is commercially available in the market, however this technology is not economic to most Malaysian farmers. It was reported that only 15 biogas and anaerobic digesters in Malaysia livestock farms with 60% are not working or in dormant status (Nurul Aini *et al*., 2018). The biogas setup cost was found to be impractical (not economic) and there is a lack of knowledge among small-medium livestock farmers which may be responsible for this low adaptation and the uptake of biogas technology. The cost of covering an anaerobic digester varies depending on the size, location, and type of renovation needed. These additional costs take a longer return of investment to the farmers. Other approaches such as simple floating biogas traps are not practical as they may be too small or not practical to farmers. However, Bio-flowt is another simple biogas trap introduced in 2019 that can fit to any anaerobic pond (Bastami and Shaari, 2020). Bio-flowt is a cheap and practical biogas trap as its mobility can be customised according to the farmers' requirement and no renovation needed on the anaerobic pond. In addition, the cost for 4 m^3 capacity Bio-flowt is only RM700 compared to others which are reported to be between RM4,500 to RM30 million (Nurul Aini *et al*., 2018). Bio-flowt as a biogas trap in anaerobic lagoon may help the country to reduce the current national GHG emission to 2.852 and 1.714 Gg yr^{-1} from dairy and beef cattle industries respectively (Ministry of Natural Resources and Environment, 2018). The uses of biogas as cooking fuel or simple flaring help in converting a potent CH_4 gas to CO_2. High volume biogas produced can possibly be used as electricity generator to supply energy to the farm facilities and machinery. It is one of the ways to save the environment from serious pollution and climate changes for the sake of the next generation. This is in line with the national policy to reduce GHG emission by 40% in 2020 compared to 2005 according to '*Rancangan Malaysia ke-11*' (11th Malaysia Plan) (Unit Perancang Ekonomi, 2015).

CONCLUSION

The covering method studied was found to be effectively reducing the potent gases emission. As much as 45.5% and 56.9% of CH_4 and NH_3 were successfully reduced by the uses of Cocopeat and Straw as the biological cover on the slurry surface respectively. Both approaches not only reduced greenhouse emissions but it may help in improving air and water quality as well as to save the cost of disposing the waste. Covering ruminant liquid waste in this study is found to be promising in manure management towards facing global warming and climate changes. Human consumption on the animal protein grows as the population increases, thus this requires immediate mitigation on all degrees to make livestock farming sustainable without growing more potent gas to the atmosphere.

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