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DAIRY MANURE AMENDMENT EFFECTS ON ODOR AND GAS EMISSIONS

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ABSTRACT Twenty-two amendments representing different modes of action were screened for odor and gas emission from dairy manure stored at room temperature (20^{o}C) for short- (3 d) and medium-term (30 d). Seven of these amendments were selected for replicated (n=2-4) study at two temperatures (10 and 20^{o}C) and three storage periods (3, 30 and 94 d). Amendment was added to 2-kg dairy slurry (1:1.7 urine:feces; 12% total solids) following the manufacturer rates. Untreated slurry was also evaluated as was a feed-through additive. Odor emissions were estimated by six qualified odor assessors following an olfactometry international standard. Odor quality characterizations included hedonic tone, supra-threshold odor intensity, and odor character. Gas emissions measured included hydrogen sulfide (H_2S), ammonia (NH_3), carbon dioxide (CO_2), methane (CH_4) and nitrous oxide. There were no consistent reductions of odor and gas emissions in the amendments and feed additive treatments for all storage periods at 20^{o}C and 10^{o}C. Average daily odor emission rates were 5 to 94 OU_E cm^{-2} d^{-1}. Significant reductions (31%; P=0.032) were measured in the abandoned mine drainage (AMD) sediment treatment after 3 d at 20^{o}C. Essential oils *Hyssopus* and peppermint reduced odor emission by 27-48% after 94 d at 20^{o}C. But for 30 d at 10^{o}C these oil treatments increased odor by 29-65%. Generally, mean gas emission rates were 1.4 to 2 times higher at 20^{o}C than at 10^{o}C (P=0.04-<0.0001). Only the AMD sediments consistently reduced NH_3 and CO_2 emissions after 30 d and 94 d (P=0.02-<0.0001). A microbial digestive treatment (powder enzymes and bacteria) reduced NH_3 emissions after 94 d (P=0.006-<0.0001) at 10^{o}C and 20^{o}C and CH_4 emissions (12%) after 30 d at 10^{o}C (P=0.005). Storing treated dairy manure for 94 d either at 10^{o}C or 20^{o}C reduced odor and greenhouse gas emissions by 88-100%. All treated and untreated manure slurries had unpleasant to extremely unpleasant smell and 76 to 100% of certified odor assessors described manure as offensive, earthy, medicinal and fishy. Odor emission was correlated to odor strength, H_2S, CH_4 and CO_2 emissions but inversely to NH_3 emission.

Keywords: Manure, amendment, feed additive, dairy, odor, gas, ammonia, methane

INTRODUCTION Dairy manure is rich in organic materials and nutrients but these can be a significant source of ammonia (NH_3), hydrogen sulfide (H_2S) and greenhouse gases

(GHG) during different stages of manure management. In dairy operations, manure handling and storage facilities can be a significant source of malodors. Due to far-reaching environmental and socio- economic concerns, efforts to reduce odor, greenhouse gas, NH_3 and H_2S air emissions from animal agriculture are essential.

One treatment approach that appears practical and economical to farmers is the use of livestock manure amendments. Amendments used to reduce odor and gas emissions are often categorized according to their modes of action: (1) digestive additives, (2) disinfecting additives, (3) oxidizing agents, (4) adsorbents, and (5) masking agents. Chemical pH adjustment amendments are also used to manage off-gas emissions. Most proprietary odor control agents are digestive additives.

Animal scientists have also included essential oils in livestock diets to control specific microbial populations and modulate rumen fermentation. The addition of plant extracts to the rumen results in an inhibition of deamination and methanogenesis, resulting in lower ammonia N, methane and acetate (Calsamiglia et al., 2007). Many investigations have proven the efficiency of essential oils as antimicrobial agents. McIntosh et al. (2003) observed that "hyperammonia-producing" bacteria were inhibited by a commercial blend of thymol, eugenol, vanillin and limonene and suggested that the main effect of these oils occurred during the final phase of protein degradation.

Many investigations on manure amendments and feed additives have been product-based and measured only odor and one or two odorant compounds from treated dairy manure. There were limited studies on the effect of product application or inclusion of feed additive on the gas emissions from dairy manure. Our study focused on simultaneous assessment of the efficacy of manure amendments and a feed additive that claim to reduce odor and/or gas emissions in dairy manure. The **objectives** of this study were 1) to evaluate performance of manure amendments and a feed additive in reducing odor, NH_3, H_2S and/or GHG air emissions in dairy manure after short (3 d), medium (30 d) and long-term (94 d) storage periods at 10^oC or 20^oC; 2) to evaluate different modes of amendment actions on the emissions; and 3) to characterize odor descriptions using human panel observations.

MATERIALS AND METHODS. Manure amendments. Twenty two manure amendments were selected for a preliminary Screening trial based on claims that the materials reduced one or more air emissions from dairy manure (n=1 for each amendment). These materials comprised five different modes of actions which include seven microbial digests, six oxidizing agents/chemicals, three disinfectants, six masking agents, and an adsorbent (details in Wheeler et al., 2010). From the 22 amendments tested, six materials were selected based on efficacy in reducing dairy manure odor and/or gas emissions, cost effectiveness, practical application, and to represent different modes of action. These six materials, and a seventh (recommended from anecdotal odor reduction performance on dairy farms), were used for the Main odor and gas emissions trial (n=2-4 per amendment). The seven odor reducing manure amendments in the Main trial consisted of one oxidizing agent (Abandoned mine drainage sediment: AMD), one chemical material (CGE liquid), one disinfectant (oxychlorine liquid), two microbial digestive additives (MBR liquid; MPG powder) and two essential oils (peppermint black mitcham; *Hyssopus*). A feed-through essential oil was also evaluated.

Manure preparation. Dairy manure was collected during a feed additive experiment at The Pennsylvania State University (PSU), Dairy Production Research and Teaching facility managed by the Department of Dairy and Animal Science (University Park, PA). Manure samples were collected separately as urine and feces from lactating dairy cows on Control diet and Feed-additive essential oil diet. Manure from Control and Feed-additive was mixed separately as 1:1.7 urine and feces ratio and stored at 4^oC for 36 d to produce stable feedstock materials. A 500 g subsample from the Control and Feed-additive manures were sent to the PSU Agricultural Analytical Services Laboratory for standard analysis. Average manure pH was 7.86 while total N, NH_4-N and organic N in dry weight manure basis was 50.6 g kg^{-1}, 4.61 g kg^{-1} and 72 g kg^{-1}, respectively. At the end of the study, pH of treated and control manure was analyzed at the surface of manure (Orion Inst.). Total solids (TS) and volatile solids (VS) were determined via oven drying standard-methods and ranged from 10.5 to 11.3% and 8.86 to 9.70%, respectively.

Laboratory incubation. Each manure amendment was added to individual 2 kg samples of dairy slurry in 3.8 L glass jars following manufacturer or researcher recommendations. Jars were "incubated" in temperature-controlled chambers for 3 d and 30 d at 20^oC for the Screening trial with the addition of 94 d during the Main trial plus all three storage durations at 10^oC during the Main trial. Untreated manure samples, as Controls, were prepared and incubated at days and temperatures identical to manure amendment treated samples. The jars were loosely sealed to avoid over pressurization during incubation period. Due to the need to limit the number of samples for odor panel evaluation per day, the treatments were prepared in five batches, which included Control (untreated) manure in each batch. The various modes of actions were randomly spread over the five batches to avoid bias. Analysis of gas and odor concentrations from 10^oC manure treatment was immediately performed one day after the analysis of 20^oC manure.

Gas measurements. The treated and control jars were removed from the incubator and placed in a multi-chamber steady-state gas emission detection system (Wheeler et al., 2007) for simultaneous gas emission measurements. Ammonia and GHG concentrations (methane [CH_4], carbon dioxide [CO_2], nitrous oxide [N_2O]) were determined by a photoacoustic multi-gas field-monitor [PAS] (Model 1412, Innova, Denmark) from each of six flux chambers every 72 min over a 24-h period. Each jar was partially immersed in a 20^oC or 10^oC water bath, matching its incubation temperature, with a continuous supply of 2 L min^{-1} filtered, moist sweep air. Two additional flux chamber jars contained distilled water as controls, a check for cross-contamination of sampling lines, and for determining background gas/odor concentrations. After the gas analysis using the PAS instrument, the same gas sample was used to estimate H_2S (TEI 450C Pulsed Fluorescence H_2S/SO_2, Thermo Environmental Instruments, Franklin, MA). Gas emission rates were computed using the following equation:

$$E = \frac{Q(C_1 - C_{BLK})}{A} \quad \text{[Eq. 1]}$$

where E is gas emission rate (mg cm^{-2} min^{-1}), Q is flow rate of filtered air supplied through each chamber (0.002 m^3 min^{-1}), C_1 is the measured gas concentration (mg m^{-3}), C_{BLK} is measured ambient gas concentration ("blank" distilled water in mg m^{-3}) and A is the surface area of manure in each chamber (cm^2). The daily gas emission (mg $cm^{-2}d^{-1}$) was computed as the sum of emission rates for 24 hours.

Odor measurements and calculations. Two to 3 hours after manure placement in the gas measurement system, approximately 7.0 L of odorous headspace gas was collected from each of the chambers into a 10 L preconditioned Tedlar™ bag for olfactory evaluations. All odor samples were presented to trained panelists and analyzed for detection threshold (DT) and recognition threshold (RT) levels using an Ac'Scent International Olfactometer (St. Croix Sensory, Inc., 2007) following the Triangular Forced-Choice method (CEN, 2003).

After use in the Olfactometer, the bag containing the odorous gas sample was moved to a different lab where each panelist would smell the undiluted bag contents and evaluate for hedonic tone and intensity. Hedonic tone (pleasantness) was subjectively quantified using a 22-unit scale (-11 for extremely unpleasant to +11 for extremely pleasant). The panelists assessed the odor intensity using the Labelled Magnitude Scale method (Green et al., 1996) and supra-threshold odor intensity (ASTM E544-99 (2004) concentrations of n-Butanol in water. All odor panel evaluations were performed within seven hours of sample collection. Odor emission was computed using Eq. 1 with the following changes in variables: E is manure odor emission rate (OU m^{-2} min^{-1}), C_1 is odor concentration of manure (OU m^{-3}), C_{BLK} is odor concentration of water blanks (OU m^{-3}). The daily odor emission (OU cm^{-2} d^{-1}) was computed by converting emission rates in min to d. In order to account for the sensitivity of certified odor assessors during odor measurement time and compare our results to other odor studies, odor emission rate was corrected using n-Butanol standards. This European odor concentration, C_{1E} (OU_E m^{-3}) was computed using equation 2:

$$C_{1E} = DT \times \frac{ODC_b}{B} \qquad \text{[Eq. 2]}$$

where DT is odor dilution threshold of gas sample, (OU m^{-3}), ODC_b is the average odor detection threshold of the last 12 n-Butanol standards evaluated by the individual assessor, (OU m^{-3}), and B is concentration of n-Butanol standard equivalent to 1 European odor unit (OU_E). Odor detection threshold of n-Butanol standard (ODC_b) was computed using Eq 3:

$$ODC_b = \frac{1000 \times C_b}{DT_b} \qquad \text{[Eq. 3]}$$

where C_b is concentration of n-Butanol (μL L^{-1}), and DT_b is odor detection threshold of n-Butanol standard (OU m^{-3}).

Statistical analysis. The main experiment had a factorial 2 x 3 design and was analyzed statistically using SAS program (SAS, 2003). For each batch of manure samples, the effect of amendment treatments, time, incubation period and the interactions of time, treatment and incubation period were included in the linear model. Probabilities of differences between treated and untreated manure samples were calculated using least square means at $P < 0.05$. Significant reductions in odor and gas emission rates after the addition of manure amendment or feed additive were calculated and analyzed using T-test procedure at P=0.45 to <0.05. Odor characteristics were analyzed using basic statistics. Relationships of odor, odor strength and gas emission rates were assessed using Pearson correlation.

RESULTS AND DISCUSSION. Preliminary Screening trial. Odor emissions were significantly different between 3 d and 30 d incubation at 20^oC (P =<0.0001). Odor emission rates ranged from 6 to 170 OU_E cm^{-2} hr^{-1} with the highest emission measured in MAE, an aerobic/facultative microbial product, and lowest in manure treated with AMD. None of the 22 manure amendments significantly reduced odor emissions from dairy manure for both 3d and 30d incubation. Products that acted as microbial digest/enzymes, disinfectant and masking agent provided significant short-term control of odor (P =<0.0001). However, after 30 d, only microbial digest/enzyme with frequent re-application retained its efficacy. For all products tested, it appears that aging the manure slurry for 30 d at 20^oC reduced malodor gas production and odor strength by 10 to 105% (P = <0.0001). Hedonic tone ranged from -2 to -6 indicating that none of the products had pleasant smell. For all amendment products, 27% to 67% of certified odor assessors reported that the treated and untreated manure gas had an earthy and offensive smell. Odor emissions were significantly correlated to odor strength of dairy manure while no relationship was found between odor emission and hedonic tone. Odor emission and intensity from dairy manure were not correlated to NH_3 gas.

None of the 22 amendments were able to simultaneously reduce NH_3, CO_2 and CH_4 fluxes from dairy manure. Ammonia emission rates ranged from 0.002 to 0.25 mg NH_3 cm^{-2} hr^{-1} while CO_2 emission rates ranged from 0.11 to 3.02 mg CO_2 cm^{-2} hr^{-1}. Methane emission rates ranged from 0.001 to 0.24 mg CH_4 cm^{-2} hr^{-1}. Average N_2O flux rates remained below 1 µg cm^{-2} hr^{-1} during the incubation periods. After 30 d of incubation, average NH_3 and CH_4 flux rates of all product treatments except MUN (liquid chemicals and surfactants for facultative bacteria) treatment were below 0.07 mg gas cm^{-2} hr^{-1}. Average CO_2 emission rates in all products were <0.58 mg CO_2 cm^{-2} hr^{-1} after a month of incubation. Six amendment products that acted as oxidizing/chemical (AMD, CAS [a chemical mixture]), masking agents (glycerol, *Hyssopus* and peppermint oils) and adsorbent (zeolite) significantly reduced NH_3 by >10% (P =0.04 – <0.0001) after 3 and 30 d incubation. Microbial digest/enzymes with N substrate (MUN) appear effective in reducing CH_4 fluxes after short- and long-term incubation but caused an increase in NH_3 emission after 30 d. Most of the masking agents and disinfectants (borax, hydrogen peroxide, oxychlorine solution) significantly produced CH_4 in both incubation periods (P =0.04 – <0.0001). The majority of test products controlled CO_2 production after 30 d and reduction ranged from 12 to 52%. For both CH_4 and CO_2 fluxes, it appears that aging the manure slurry for 30 d at 20^oC significantly reduced gas production by 11 to 100% (P = <0.0001). While some products provided short-term reduction of gas and others after a longer period, our results show that the efficacy of 22 amendments to mitigate gas emissions from dairy manure is finite and requires re-application. Based on the results of the Screening trial the six amendments (plus one unscreened product) for the main experiment were chosen, although, some of these materials caused an increase in odor emission after 3d (MBR an oxychlorine solution) and 30 d (essential oils) incubation.

Main experiment. After 94 d of incubation at 10^oC and 20^oC, the pH of treated manure slurry ranged between 6.77 to 8.62 with the lowest pH measured in AMD treatment and highest in microbial digest MPG treatment. The 2 unit pH decrease of AMD-treated slurry was due to H^+ production following hydrolysis of ferric iron (Castillo-Gonzalez and Bruns, 2005). Average manure slurry pH of untreated samples was 8.16 after 94 d for both temperatures. There was a slight decrease in total solids after 94 d of storage in the liquid-amendment treated slurry probably due to further decomposition of organic material by microbial communities in the manure slurry. Average total solid was 9.1% for the control and 8.7% for liquid-treated manure slurry. Due to the addition of flocculating sediments, total solid was 16% in the AMD treatment after 94 d.

Odor. Some amendments reduced odor depending on incubation periods, temperature and frequency of applications. Average daily odor emission rates were 5 to 94 OU_E cm^{-2} d^{-1}. Among treated manure samples, the highest odor emission was measured in the feed additive and microbial digest MPG treatments and lowest emission in manure treated with digestive MBR. Perschbacher-Buser et al. (2005) found higher odor emission rates and lower hedonic tone (more unpleasant) of five commercial odor control additives (microbial digests and chemicals) than untreated at 9-d and 144-d incubation periods at 21°C, concluding that these products were not effective.

In all treatments, average daily odor emission rates peaked at 3 d incubation (52-94 OU_E cm^{-2} d^{-1}) for both 10°C and 20°C and were below 37 OU_E cm^{-2} d^{-1} at 94 d. There was significant reduction (73%; $P<0.0001$) of odor emission rates in all treated and untreated samples after 94 d incubation. Between 10°C and 20°C, odor emission rates were significantly high in warm condition ($P= 0.03\text{-}<0.0001$). It appears that long term storage of manure slurry at 20°C could reduce odor emission rates provided that there is no addition of manure during that period. Among all amendments tested, highest significant reduction (31%; $P=0.032$) of odor emission rates were measured in the AMD treatment at 3 d 20°C condition. AMD contains iron(III) hydroxide ($Fe(OH)_3$) a highly acidic material. In a study of $FeCl_3$ on degradation of odorous compounds, Castillo-Gonzalez and Bruns (2005) reported a significant reduction of volatile fatty acid concentrations (propionic butyric, isobutyric, valeric and isovaleric) in swine manure between 2 and 6 d incubation at 25°C. The microbial digestives MBR and MPG and chemical CGE significantly reduced odor by 26-47% at 20°C when treatments of manure slurries were continued for 30 d (P=0.10-0.05). Because these materials were added weekly or biweekly to dairy manure, it appears that these materials offered effective odor control after 2 to 4 applications. Heber et al. (2001) studied 35 additive products to swine manure where none of the additives reduced odor dilution threshold after 42 d at 20°C. In contrast, Zhu et al. (1997) reported that five swine commercial amendments (microbial digest and chemicals) significantly reduced odor thresholds 58 to 78% after 35 d.

Significant increase in odor emission rates (22-65%; P=0.000-0.011) were measured in manure treated with essential oils (*Hyssopus* and peppermint oils) and microbial digestive MPG after 30d at 10°C along with a significant increase in odor intensity in essential oil treatments (P=0.004-0.05). It is likely that the scent of *Hyssopus* and peppermint oils added to odor measured in these treatments. The majority of assessors described these treatments as one of the most favorable unpleasantness scales (-0.5) in all treated samples incubated at 10°C. Also, only 56% of assessors reported the essential oil treatment as offensive odor compared to 70% of assessors who reported offensive odor for untreated manure. Although essential oils added odor during storage periods under cool condition, the quality of odor emitted is unlikely a nuisance because of relatively favourable aroma of oils.

Average odor intensities in all treatments and storage periods were highly variable for both 10°C and 20°C. Estimated odor intensity was between 412 and 2,831 ppm n-Butanol in water with the highest odor intensity measured in MPG treatment and lowest in the

AMD treatment. AMD reduced odor strength (6%) after 30d at 10^{o}C (P=0.02-<0.0001). It was found that none of the 7 amendments or feed additive after prolonged storage at 10^{o}C or 20^{o}C reduced odor strength by >10%. All certified assessors reported an unpleasant odor for all treated and untreated samples with hedonic tone between -0.20 and -10 in all treatments. Interestingly, among treated manures, several assessors reported pleasant scale of +1.1 for peppermint oil treated manure after 30d at 20^{o}C. For untreated manure slurries, 76 to 100% of certified assessors described the odor as offensive, earthy, medicinal and fishy regardless of temperature and incubation periods. These descriptors were also reported by assessors for manure treated with microbial digest, oxidizing agent, feed additive and disinfectant amendments. Fruity character was reported by 59 to 94% of assessors in addition to the four odor descriptors above for manure treated with chemical CGE and essential oils. The descriptors reported by trained assessors in this study reflect the compositions of amendments and characteristic of odor in treated manure. This is important in the overall evaluation and mitigation of odor emitted from treated dairy manure. Concentration of n-Butanol in water as a measure of odor intensity was significantly correlated to odor emission rates in dairy manure. This shows that the higher the odor intensity the higher the odor emission from dairy manure. Odor intensity was correlated to NH_3, CH_4 and CO_2 emissions.

Gases: Similar to odor, there were no consistent reductions of NH_3, H_2S and GHG gases from dairy manure in all treatments, incubation periods and temperatures. The seven amendments were only effective in reducing gas emissions depending on storage periods and incubation temperatures. Generally, mean gas emission rates were 1.4 to 2 times higher at 20^{o}C than at 10^{o}C (P=0.04-<0.0001). In all treatments except AMD, there was an increase of NH_3 emission rates in manure slurries after 94 d of incubation for both 10^{o}C and 20^{o}C. An increase in NH_3 emissions could have been due to increase supply of NH_4^+-N from the decomposition of organic materials in manure by bacterial community or continued supply of organic substrates as bacterial cells die in the case of antimicrobial agents such as essential oils. Also, more ammonia gases were volatilized at 20^{o}C because of increase in the rate of microbial activities under warm conditions. Average daily NH_3 emissions were 0.59-2.84 mg NH_3 cm^{-2} d^{-1}. Among all treated manure, only AMD consistently reduced NH_3 emissions (33-95%) after 30 d and 94 d (P=0.02-<0.0001) while MPG treatment reduced NH_3 emissions (9-18%) after 94 d (P=0.006-<0.0001) for both warm and cool conditions. The decrease in ammonia emission in AMD treatment could have been due to inhibition of ammonia producing bacteria under acidic environment. Also, manure treated with microbial digestives and essential oils significantly reduced NH_3 emission after 94 d (P=0.10-<0.0001) at 10^{o}C. Similar results were reported by Van der Stelt et al. (2007) in which a significant decrease of 34% in NH_3 volatilization was observed under two microbial treatments when the manure was stored at 4^{o}C and without mixing. For all other gases, our emission rates decreased after 94 d storage in all treatments for both temperatures.

Average methane emission rates were <0.59 mg CH_4 cm^{-2} d^{-1} in all treatments, storage periods and conditions. Methane emission rates peaked after 3 d with highest emission rates measured in MPG and feed additive treatments and lowest rates in the AMD. Generally, CH_4 emissions continued to decline (by 2 to 150 times) after 94 d of incubation for both 10^{o}C and 20^{o}C in treated and untreated manure slurries. After short term storage period in all temperatures, none of the amendments tested significantly reduced CH_4 emissions. Only the microbial digestive MPG significantly decreased (12%)

CH_4 emission after 30 d at 10^oC (P=0.005). There was a significant production of methane gas in the chemical CGE and microbial digestive MBR treated manure after 94 d under warm condition.

Mean daily CO_2 emission rates were significantly different among three storage periods and between 10^oC and 20^oC with rates from 4 to 17 mg CO_2 cm^{-2} d^{-1} in all treatments (P=0.005-<0.0001). After 94 d, CO_2 emission rates were significantly reduced in all treatments (P=0.005-<0.0001). A significant increase in the CO_2 emission rate (21-34%) was measured in manure slurries treated with essential oils, microbial MBR and chemical CGE amendments after 94 d incubation at 10^oC (P=0.001-0.01). Perhaps, the addition of these materials to manure slurries stimulates microbial processes even under cool conditions. AMD treatments consistently and significantly reduced CO_2 emission rates after 30 d and 94 d at 10^oC and after 3 d and 30 d at 20^oC (P=0.02-<0.0001).

Nitrous oxide emission rates remained <2 μg N_2O cm^{-2} d^{-1} in all treatments and conditions and were 761 times lower than NH_3 emission rates. Nitrous oxide emission rates remained relatively higher in feed additive treatments than untreated manure in all storage periods at 20^oC. Generally, there were no consistent reductions of N_2O gas observed in any treatments in this study due to a very low emission rates during incubation.

Hydrogen sulfide emission rates remained below 3.4 μg H_2S cm^{-2} d^{-1} in all treatments, incubation periods and conditions. There were significant reductions of H_2S emission rates (80%) after 94 d at 20^oC in the manure slurries treated with essential oils (P=0.01). Several laboratory studies have indicated plant oils effectively reduce fermentation in stored cattle and swine wastes (Varel and Miller, 2001, 2004; Varel et al., 2006). The essential oils acted as antimicrobial agents in manure in which they terminate bacterial growth or produce substrates that inhibit the production of H_2S. After our 94 d incubation period, H_2S gas was barely detectable (0.07 μg H_2S cm^{-2} d^{-1}) in all treatments and controls.

Correlations between gas and odor: Emission rates of NH_3, CH_4, and H_2S were significantly and highly correlated to odor (P=0.01-<0.0001). However, only CH_4 and H_2S gases were positively correlated to odor emissions. Being an odorous gas, it is expected that high H_2S emission rate leads to high odor emissions. However, for odorless CH_4 gas, emission rate was also directly correlated to odor. One explanation is that the production of odor may occur under similar anoxic conditions and microbial processes for methanogenesis. In contrast, an odorous gas such as NH_3 had an inverse relationship with odor emission. High odor emission rates were measured in treatments with low NH_3 emissions. This shows that the malodor emitted from dairy manure may not be necessarily from NH_3 gas but from volatile organic compounds in addition to H_2S that are produced largely from decomposition/fermentation of organic materials.

Summary. *Hyssopus* and peppermint oils reduced odor emission by 27-48% and H_2S emission by 78-81% after long term storage of dairy manure at warm 20^oC conditions. However, after 30 d storage at 10^oC these essential oil treatments increased odor by 29-65% and H_2S by 60-131%. As antimicrobial agents, essential oils have been shown to accumulate in cell membranes and disrupt their integrity, thus leading to a leakage of enzymes and metabolites (Smid and Gorris, 1999). It is likely that during short-term storage of manure with essential oils, growth of some microbial strain was inhibited. And as incubation proceeds, components of bacterial cells leaked out and became available for reduction/fermentation. The feed –additive essential oil did not reduce odor emissions but NH_3 emissions decreased after long-term storage at 20°C. AMD reduced odor after short-term storage while microbial digestives (MBR and MPG) reduced odor after medium term storage (30 d) at warm condition. Also, after weekly or biweekly applications of microbial digestive to dairy manure, there was a substantial reduction of NH_3 emission rates after short-term storage at 10°C. The reduction of odor and NH_3 emissions after frequent applications to manure suggests a long period is needed for the materials to become fully activated and reach dominant levels for degradation processes. However, frequent application of these amendments to manure may not be practical to a dairy farm because large amounts are necessary to become effective odor and gas controls. Based on the results of this study, there was no single mode of action that effectively reduced odor and gas emissions in dairy manure. In fact, the presence of these materials in dairy manure causes an increase of one or two gases after storage periods such as the case of chemical CGE and essential oil treatments in the CH_4 and CO_2 production. None of the test materials reduced CH_4 after short term incubation period. For CO_2 emission control, AMD sediments reduced CO_2 gas after medium-term storage for both 10°C and 20°C. In order to be efficient in reducing odor and one or more gas emissions in dairy manure, it requires a manure amendment that inhibits production of volatile organic compounds or shifts microbiological or chemical processes of organic compounds to less odorous forms.

CONCLUSIONS None of the seven amendments or the feed additive consistently reduced odor and gas emission rates in dairy manure after short and long-term incubation at 10 and 20°C. Several amendments significantly reduced odor and gas emissions depending on incubation periods, temperature and frequency of applications. The addition of *Hyssopus* and peppermint oils were effective for long-term odor control while abandoned mine drainage (AMD) sediment was effective for short-term odor control under warm condition. Under long-term cool condition, only the microbial digest MBR and chemical CGE offered effective odor and H_2S emissions control. Generally, the feed through additive treatment for dairy cows was not an efficient method for odor emission control in this study but showed potential for NH_3 emission control at warm conditions. The AMD sediments decreased NH_3 emissions for both medium and long-term storage periods and decreased CO_2 after medium-term storage. Storing dairy manure for 94 d either at cool or warm condition reduced odor and GHG emissions by 88-100%. None of the manure slurries treated with test amendments had pleasant smell. Most odors as described by certified assessors were offensive, earthy, medicinal and fishy. Odor emission was correlated with odor strength and gases such as H_2S, CH_4 and CO_2 emission but inversely related to NH_3 emission. In order for the amendment to offer effective odor and gas control, it is essential that the material is quick acting, inexpensive, not a source of odor and gas emissions, and either enhances organic substrates degradation or reduces the production of volatile organic compounds in dairy manure.

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REFERENCES

ASTM. E544 – 99 (2004).Standard practices for referencing suprathreshold odor intensity. In Annual Book of ASTM Standards. West Conshohoken, PA 19428. American Society for Testing Materials.

Calsamiglia, S., M. Busquet, P. W. Cardozo, L. Castillejos and A. Ferret. 2007. Invited Review: Eessential oils as modifiers of rumen microbial fermentation. J. Dairy Sci. 2007. 90:2580-2595

Castillo-Gonzalez, H. and M.A. Bruns. 2005. Dissimilatory iron reduction and odor indicator abatement by biofilm communities in swine manure microcosms. Applied and Environ. Microbiology 71(9): 4972-4978.

CEN.2003. Air quality – Determination of odour concentration by dynamic olfactometry. EN. 13725 European Committee for Standardization (CEN), Management Centre: Rue de Stassart 36, B-1050 Brussels.

Green, B., P. Dalton, B. Cowart, G. Shaver, K. Rankin, and J. Higgins. 1996. Evaluating the "Labeled Magnitude Scale" for measuring sensations of taste and smell. Chem. Senses 21(3) :32-334.

Heber, A.J., Ni, J, Sutton, A.L., Patterson, J.A., Fakhoury, K.J., Kelly, D.T. , and P. Shao. 2001. Odor Solution Initiative Testing Results manure pit additives. C.L. Tengman, A.K. Gralapp and R.N Goodwin (eds). National Pork Board, Des Moines, IA USA, 191 pp.

McIntosh, F. M., P. Williams, R. Losa, R. J. Wallace, D. A. Beever, and C. J. Newbold. 2003. Effects of essential oils on ruminal microorganisms and their protein metabolism. Appl. Environ. Microbiol. 69:5011–5014

Perschbacher-Buser, Z.L., Parker, D.B., Rhoades, M.B., and D.L. Williams. 2005. Moisture content and commercial additive effects on odor emissions from simulated feedlot pen surfaces and lagoons. ASAE Annual Intl Meeting, 2005, Paper No. 054072.15 pp.

SAS. 2003; SAS/STAT user guide. Version 9.1, SAS Institute, Cary, NC.

Smid, E.J. and L.G.M. Gorris.1999. Natural antimicrobials for food preservation. In: Handbook of food preservation. Eds. M.S. Rahman. Marcel Dekker, New York, NY. pp. 285-308.

St. Croix Sensory, Inc. 2005. A review of the science and technology of odor measurement. Prepared for the Iowa Department of Natural Resources. Lake Elmo, MN. Available on line at: http://www.iowadnr.gov/air/afo/files/odor_measurement.pdf (confirmed 6/04/08)

Van der Stelt, B., Temminghoff, E.J.M., VanVliet, P.C.J., W.H. Van Riemsdijk. 2007. Volatilization of ammonia from manure as affected by manure additive, temperature and mixing. Bio.Tech. 98:3449-3455.

Varel, V.H. and D. L. Miller. 2004. Eugenol stimulates lactate accumulation yet inhibits volatile fatty acid production and eliminates coliform bacteria in cattle and swine waste. J. Applied Microbiology 97:1001-1005.

Varel, V.H. and D.N. Miller. 2001. Plant-derived oils reduce pathogens and gaseous emissions from stored cattle waste. Applied and Environ. Microbiology. 67(3):1366-1370.

Varel, V.H., Miller, D.N., and E.D. Berry. 2006. Incorporation of thymol into corncob granules for reduction of odor and pathogens in feedlot cattle waste. J. of Animal Sci. 84:481-487.

Wheeler, E.F., M.A.A Adviento-Borbe, R.C. Brandt, P.A. Topper, D.A. Topper, H.A. Elliott, R.E. Graves, A.N. Hristov, M.A. Bruns and V.A. Ishler. 2010. Amendments for mitigation of dairy manure ammonia and greenhouse gas emissions: Preliminary screening. ASABE Annual International Meeting, Pittsburgh, PA.

Wheeler, E. F., P. A. Topper, N. E. Brown and G. A. Varga. 2007. Multiple-chamber steady-state gas emission detection from dairy manure slurry. CD-ROM Proceedings of International Symposium on Air Quality and Waste Management for Agriculture. ASABE Publication Number 701P0907cd, St. Joseph, MI.

Zhu, J., Bundy, D.S., Li, X., and N. Rashid. 1997. Controlling odor and volatile substances in liquid hog manure by amendment. J. Environ. Qual. 26:740-743.