Manure amendments for mitigation of dairy ammonia and greenhouse gas emissions: preliminary screening

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Abstract: Amendments can be practical and cost-effective for reducing ammonia [$NHRR_3$] and greenhouse gas [GHG] emissions from dairy manure. In this study, the effect of 22 amendments on NH_3 and GHG carbon dioxide [CO_2], methane [CH_4] and nitrous oxide [N_2O] emissions from dairy manure were simultaneous investigated at room temperature (20℃). Dairy manure slurry (2 kg; 1:1.7 urine: feces; 12% total solids) was treated with various amendments, representing different classes of product, following the suppliers' recommended rates. In this screening of products, one sample of each amendment was evaluated along with untreated manure slurry with repeated measurements over 24 h. Gas emissions were measured after short (3 d) and medium (30 d) storage duration using a photoacoustic multi-gas analyzer. Six amendment products that acted as microbial digest, oxidizing agent, masking agent or adsorbent significantly reduced NH_3 by >10% (P = 0.04 to <0.001) after both 3 and 30 d. Microbial digest/enzymes with nitrogen substrate appeared effective in reducing CH_4 fluxes for both storage times. Most of the masking agents and disinfectants significantly increased CH_4 in both storage periods (P = 0.04 to <0.001). For both CH_4 and CO_2 fluxes, aging the manure slurry for 30 d significantly reduced gas production by 11 to 100% (P<0.001). While some products reduced emissions at one or both storage times, results showed that the ability of amendments to mitigate emissions from dairy manure is finite and re-application may be required even for a static amount of manure. Simultaneous measurement of gases identified glycerol as a successful NH_3 reduction agent while increasing CH_4 in contrast to a digestive-microbial product that significantly reduced CH_4 while enhancing NH_3 release.

Keywords: methane, greenhouse gas, emission, amendment, additive, dairy manure, ammonia, mitigation

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1 Introduction

Intensive farming methods have proven economically effective, yet handling animal waste from dairy farms can have adverse impact on the environment even when well-managed. One challenge is the emission of

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naturally occurring ammonia [NH_3] and greenhouse gases (GHG: nitrous oxide [N_2O], carbon dioxide [CO_2], methane [CH_4]) from manure storage. Current technology provides a wide array of innovative treatments to reduce gas and odor emissions, including: vegetative shelterbelts, anaerobic digestion, efficient dietary management strategies, solids separation, and the use of manure amendments (MWPS, 2008).

Use of manure amendments is a management approach that often appears practical and economically viable to farmers. An amendment can be defined as a substance that is applied to an animal waste with the intention of alleviating one or more of the problems associated with handling and management. McCrory and Hobbs (2001) categorized commercial additives according to their modes of action i.e. (1) digestive additives, (2) disinfecting additives, (3) oxidizing agents, (4) adsorbents, and (5) masking agents. Odor control is often the primary goal of amendment use, but with increasing pressure on dairy farms from regulatory agencies to reduce GHG and NH_3 release, there is increased interest in mitigating these gas emissions.

Many manure amendments, encompassing the various modes of action, have a history of on-farm use and anecdotal reports of success in odor or gas reductions. Several of these additives cause an increase in total solids in manure storage (i.e. adsorbents) or inhibit the natural degradation of solids by the indigenous microbial population (i.e. disinfectants). Strong oxidizing agents act as disinfectants through their abilities to degrade enzymatic proteins and oxidize sulfides, mercaptans, and NH_3. One of the most widely investigated oxidizing agents is hydrogen peroxide (H_2O_2). Cole et al. (1976) found that hydrogen peroxide was effective in reducing odor offensiveness and H_2S emissions in liquid pig slurry when applied at 500 mg/L.

In contrast to on-farm experiences are controlled laboratory studies that often document poor odor and gas reduction performance for manure amendments. In a lab study of 35 manure products, Heber et al. (2001) reported 11 additives that had 95% certainty of NH_3 and/or hydrogen sulfide [H_2S] reductions when applied to swine manure but none of the additives reduced odor dilution threshold. Notably, Van der Stelt et al. (2007) found no significant decrease in NH_3 emissions in livestock manure amended with *Euro Mest-Mix* [adsorbing clay minerals]; *Effective Microorganisms* [microbial inoculant bacteria: yeast, photosynthetic and lactic acid] or *Agri-Mest* [mineral blend]). Even though an amendment successfully reduced certain odorants (e.g. NH_3 or H_2S), the overall odor may not be reduced.

Natural clinoptilolite, an ammonia-binding zeolite, has been shown to enhance adsorption of volatile organic compounds (VOC) and odor emitted from animal manure due to its high surface area. Cai et al. (2007) reported reduction>51% for selected offensive odorants (i.e. acetic acid, butanoic acid, iso-valeric acid, dimethyl trisulfide, dimethyl sulfone, phenol, indole and skatole) in poultry manure with a 10% zeolite topical application. Ammonia emission increased in studies conducted by Amon et al. (1997) where there was also no statistical reduction in odor concentration or odor emission rate for clinoptilolite-treated poultry manure as compared to control. It is believed that the frequent poor performance of absorbents in removing particular compounds stems from selective odorant adsorption, leaving other noxious odors and pollutant gases to escape. Considering zeolite impact on CH_4 emissions, Tada et al. (2005) tested various zeolites during anaerobic digestion conditions (35℃) of organic sludge for their ammonium−N (NH_4^+−N) removal benefit in an attempt to enhance methane production. Tada et al. (2005) observed four times more CH_4 production than control (untreated sludge) when 5% to 10% mordenite, a natural zeolite, was applied to organic sludge while no enhanced methane production was found in natural clinoptilolite and a synthetic H-type zeolite 3A treated sludge, even though all the tested zeolites removed NH_4^+−N to the same level.

Selected essential oils have been found to be effective antimicrobial agents, in addition to acting as odor masking agents. Aside from use as a manure amendment, animal scientists have included essential oils (plant extracts) in livestock diets to control specific microbial populations and modulate rumen fermentation. Calsamiglia et al. (2007) found that addition of plant extracts to the rumen resulted in an inhibition of deamination and methanogenesis, resulting in lower ammonium-N, CH_4, and acetate formation. In a field study, Jelínek et al. (2004) reported a 68% reduction of NH_3 emissions in cattle slurry treated with *Amalgerol* (blend of vegetable and sea-algae oils and extracts).

The use of alkaline materials such as cement kiln dust, lime, or other alkaline by-products can increase the pH to above 12.0, where few bacteria can survive. Lee et al. (2007) observed that addition of 1% of monocalcium phosphate to swine manure suppressed NH_3 emissions by 81% but was ineffective in controlling H_2S emissions for 30 hrs following application. When chemical pH amendments were applied, Massé et al. (2004) found a small methane peak (0.15%) with swine manure stored between 30 d and 60 d in an open-system (aerobic), and 2 to 22% (vol/vol) CH_4 content in closed-system (anaerobic).

1.1 Study objectives

Despite the inconsistent performance of commercial manure additives, these products continue to be widely available and popular. Numerous studies have investigated amendment performance with swine manure and poultry manure/litter. Relatively few studies have focused on dairy manure amendments. This study investigated the efficacy of manure amendments that claim to, or have potential to, reduce NH_3 and greenhouse gas emissions in dairy manure storage. An overarching goal was to evaluate as many products as practicable, representing the full array of product *modes-of-action* (classes). The primary objective of this study was to simultaneously monitor performance of amendments in reducing NH_3, CO_2, N_2O and CH_4 emissions from dairy manure after short (3 d) and medium (30 d) storage at 20℃. This was a screening of potential products for a follow-up study that evaluated the six most promising manure amendments with replicated samples at three storage times and two storage temperatures (Wheeler et al. 2010b). Evaluations were simultaneously conducted on odor emissions (not reported here) from these manure amendments (Wheeler et al., 2010a; b; Wheeler et al. 2011).

2 Materials and methods

2.1 Manure amendments

Twenty two manure amendments were selected for this screening study based on claims or reports that they reduced gas emissions from dairy manure. Most were commercially available products. Abandoned (a.k.a. acid) mine drainage [AMD] sediment and glycerol were evaluated based on anecdotal claims of emission reduction, along with selected essential oils that were undergoing evaluation for rumen gas production in a dietary trialTT. The 22 materials comprised five different classes of products that included seven microbial digest products, six oxidizing agents/chemicals, three disinfectants, six masking agents, and an adsorbent. Table 1 describes all the products tested and the corresponding rates and methods of application for stored dairy manure.

Manufacturers of each compound were contacted for a recommended rate of application based on conditions of this experiment. Some amendments required repeated reapplication per manufacturer directions (weekly for MBR, CBP and CGE). This experiment did not attempt to fully simulate manure storage conditions, particularly since there was no continual addition of fresh manure to the storage vessels. Application rates for non-commercial compounds were calculated based on anticipated chemical and/or biological activity of the compound under conditions of this study (Table 1).

One constraint on the project protocol was a resource- and logistical-limitation on the number of samples that could be evaluated simultaneously. The multi-vessel steady-state flux chamber system used for gas emission monitoring (described below) and odor sample acquisition imposed a practical upper limit of eight samples per session. For this screening of amendments, one sample (n=1) of each amendment was prepared for simultaneous quantification of odor and gas emissions.

Gas emission was determined repeatedly over a 24 h period (n=20) for each manure/amendment treatment. This approach permitted evaluation of almost two-dozen amendments versus replicated screening of only a few amendments (the latter conducted in a follow-up study [Wheeler et al. 2010b]).

Table 1 Description of twenty-two manure amendments used in the dairy manure gas (and odor) mitigation experiment.

Mode of action	Product code/material name[1] (Product form)	Product active ingredient(s)	Rate of application[2] (Method[3])
Microbial	MBR=Bio-Regen Animal Waste (liquid)	Proprietary aerobic/facultative microbes	190 µL of product diluted to 5 mL with water to 2 kg manure slurry weekly (mixed)
	MUN =UNLOK (liquid)	Proprietary chemicals and surfactants for facultative bacteria	40 mL of product to 2 kg manure slurry (mixed)
	MAE=Alken Enz-Odor 5 (coarse powder) & Alken Enz-Odor 9 (liquid) MAC=Alken Clear-Flo 8000 (coarse powder) MAF=Alken Clear-Flo 7110 (coarse powder) & Alken Enz-Odor 5 & 9	Proprietary aerobic/facultative microbes with growth factors	200 mg of Alken Enz-Odor 5 /Alken Clear-Flo 8000/ Alken Clear-Flo 7110, and 62.5 µL of Alken Enz-Odor 9 diluted in 2 to 4 mL warm water to 2 kg manure slurry (mixed)
Chemical	CBP=Biostreme 222 Pond-X (liquid) CBS=Biostreme 101 (liquid)	Proprietary chemicals/ micronutrient concentrate	20 mL (200 ppm) of 1% solution of product to 2 kg manure slurry weekly (mixed)
	CGE=Greaseater (liquid)	Proprietary mixture of chemicals in isopropyl alcohol	0.4 mL diluted to 20mL with water to 2 kg manure slurry weekly (mixed)
	CAS=Air solution R305 deamine (liquid)	Proprietary mixture of chemicals	12 mL of 1% strength of product per 2 kg manure slurry (mixed)
	CPR=Predator (liquid)[4]	Proprietary complex triazine mixture	200 µL of product per <10 ppm H_2S in manure (surface)
	AMD=Abandoned (acid) mine drainage sediments (very coarse powder)[5]	Iron-rich sediments accumulated in streams near abandoned coal mines	50 g of acid sediments to >10% total manure solids to 2 kg manure slurry (mixed)
	CSE=Septi-sol (liquid)	Proprietary dipole dibase formulation	0.1 mL of product diluted to5 mL with water to 2 kg manure slurry (surface)
Disinfectant	Borax (powder)	Sodium tetraborate decahydrate	20 g borax to 2 kg of manure slurry (surface)
	Hydrogen peroxide (liquid)[6]	Hydrogen peroxide	153 mL of 30% H_2O_2 to 2 kg manure slurry (mixed)
	Anthium dioxcide (liquid)[7]	5% aqueous stabilized chlorine dioxide (oxychlorine)	1.41 mL of product to 2 kg manure slurry (surface)
Masking	Carvacrol + pinene (liquid)	Essential oils of *Origanum vulgare* (oregano) and *Pinus sylvestris* (pine)	Dissolve 24.04 µL carvacrol and 7.80 µL pine to 1 mL of ethanol and diluted to 12.3 mL water. Add solution to 2 kg manure slurry (mixed)
	Eugenol (liquid)	Essential oil of *Syzygium aromaticum* (clove)	Dissolve 29.49 µL eugenol to 12.3 mL water and add to 2 kg manure slurry (mixed)
	Glycerol (thick liquid)	Glycerin	20 g glycerol to 2 kg manure slurry (mixed)
	Ocimum basilcum (liquid)	Essential oil of *Ocimum basilicum* (basil)	31 µL of basil to 2 kg manure slurry (mixed)
	Peppermint black mitcham (liquid)	Essential oil of *Mentha piperita* (Peppermint)	35 µL of peppermint to 2 kg manure slurry (mixed)
	Hyssopus officinalis (liquid)	Essential oil of *Hyssopus officinalis*	32 µL of Hyssopus to 2 kg manure slurry (mixed)
Adsorbent	Zeolite (powder)	Clinoptilolite, K-Ca-Na aluminosilicate	201.5 g on 2 kg manure slurry (surface)

Note: 1 Product names in bold letters were used in the follow-up replicated experiment (Wheeler et al. 2010b).

2 Recommended rate of application was based on 30 d incubation period and 2 kg dairy manure in a 3.8 L jar with manure surface area of 0.0161 m^2 and total manure solids content of 12.1%.

3 Method of application: "mixed" with manure slurry for one-minute with mechanical mixer or "surface" applied

4 CPR rate dependent upon target gas and environment variable at 0.06-0.10 L × H_2Sppm × 10,000 m^3/d airflow. Max 10 ppm H_2S assumed for this experimental slurry.

5 AMD rate based on lab experiment (Castillo-Gonzalez and Bruns, 2005) for manure slurry solids >10% requires 10 g Fe per 1% solid content.

6 Hydrogen peroxide rate determined from Clanton, Nicolai and Schmidt (1999) lab H_2S reductions.

7 Anthium dioxcide at 40 ppm achieved within slurry.

2.2 Manure preparation

Dairy manure was collected during a feed additive experiment at The Pennsylvania State University (PSU) Dairy Production Research and Teaching Facility (University Park, PA). Manure was collected as urine and feces from lactating dairy cows on the control diet. Manure slurry was immediately prepared as 1:1.7 urine-to-feces ratio (12.1% total solids; pH 8.30) to better reflect the actual partitioning of manure from lactating dairy cows (Agle et al. 2010; Morse et al. 1994). This manure slurry was then stored at 4℃ for 15 d to produce stable feedstock material. The PSU Agricultural Analytical Services Laboratory conducted standard nutrient analysis, plus pH, of a 500 g subsample from the fresh and aged batches of prepared manure slurry. Aged feedstock manure pH was 7.83 while total-nitrogen (N), ammonium-N and organic-N in dry weight manure basis was 48.9 g/kg, 24.1 g/kg and 24.8 g/kg, respectively. This manure feedstock had average (*n*=3) total solids and volatile solids (ASTM 2001, 2008) levels of 11.5% and 9.6%, respectively. At the end of the study (30 d), treated and control manure was analyzed within our laboratory at 1 mm below the surface of manure with a pH electrode (SympHony SB 301 pH meter, Beverly, MA USA).

2.3 Laboratory storage

Each amendment was mixed or surface applied to individual 2 kg samples of aged dairy slurry in 3.8 L glass jars following manufacturer recommendations or researcher calculations (Table 1). Jars were stored in a walk-in, temperature-controlled chamber for 3 d and 30 d at 20℃. Untreated manure samples (Control) were prepared and incubated identical to manure amendment-treated samples, in the same chamber. The jar lids were loosely sealed during the storage period to avoid over-pressurization from off-gases. Each jar lid used during storage was replaced with another lid during the emission measurement to control air flow rate entry into the each jar (see next section). Manure samples were not disturbed between storage and gas emission evaluations since the flux chamber gas detection system (described below) accommodated use of the storage jars. The treatments were prepared in five batches, with a Control manure sample included in each batch, because the *aged* manure feedstock exhibited significant emission variations during preliminary trials. The timing of sample treatments was staggered to achieve consistent incubation age on evaluation days, per the study protocol. The various classes of amendments were randomly spread across the five batches to avoid bias. Batches were evaluated on sequential days using the same instrumentation.

2.4 Gas measurements and calculations

A multi-chamber emission detection system was used under temperature-controlled conditions for measurements from Control and amendment-treated samples (Wheeler et al., 2007). This instrumentation system had eight identical flux chambers constructed of 3.8 L glass jars (same jars containing stored manure samples) with tight-fitting Teflon™-lined lids integrating an inlet air distribution ring. Each chamber had calibrated, flow-metered (Visi-Float® VFB 65-BV; 3% accuracy full-scale; Dwyer Instruments, Michigan City, IN), sweep air provided to the headspace above each sample during the emission testing. Calibration of the flow meters was done prior to each data collection (Agilent, Optiflow 650 digital flow calibrator, 5.0 – 5,000 mL/min, Santa Clara, CA). Customized LabVIEW™ computer software (National Instruments, Austin, TX) controlled the gas sampling sequence via relay and solenoid valve (to analyzer or exhaust). Ammonia and GHG concentrations were measured using a photoacoustic multi-gas field-monitor (Model 1412, Innova Air Tech Instruments, Ballerup, Denmark). Detection limits were: CH_4 0.1 ppm; CO_2 5.1 ppm; NH_3 0.2 ppm; N_2O 0.03 ppm. Interferences with water vapor (for measuring NH_3, CH_4) and carbon dioxide (for measuring N_2O) were automatically compensated within the instrument. Calibrations were conducted annually per manufacturer instructions by California Analytical Instruments (Orange, CA) at expected gas ranges for manure measurements. Each of the eight flux chamber jars were monitored every 72 min over a 24 h period (*n*=20 each jar). Each jar was partially immersed in a 20℃ water bath, matching its storage temperature, so that emissions were monitored at a stable, controlled temperature over the monitoring period. Each flux chamber jar was continuously supplied with 2 L/min filtered, moist sweep air. Two flux chamber jars contained distilled water as “blanks”, a check for cross-contamination of sampling lines, and for determining background gas concentrations. All emissions are reported at standard conditions (20℃; 101.325 kPa). Gas emission rates were computed using the following equation:

$$E = \frac{Q(C_1 - C_{blk})}{A} \tag{1}$$

Where, E is gas emission rate of NH_3, CO_2, CH_4 or N_2O, (mg/(cm^{-2} •min)); Q is metered flow rate of filtered air supplied through each chamber (0.002 m^3/min); C_1 is the measured gas concentration (mg/m^3); C_{blk} is measured ambient gas concentration (distilled water "blank" chamber in mg/m^3) and A is the surface area of manure in each chamber (cm^2).

2.5 Statistical analysis

The experiment was analyzed statistically using SAS program (SAS, 2003). For each batch of manure samples, the effect of amendment treatments (n=1 sample; n=20 repetitions over 24 h), storage period (3 d or 30 d) and the interactions of treatment and storage period on gas emission rates were included in the linear model. Probabilities of differences in gas emissions between treated and untreated manure samples were calculated using least square means at P<0.05. Significant reductions in gas emission rates after the addition of manure amendment were calculated and analyzed using T-test procedure at P<0.05.

3 Results and discussion

In all amendment treatments and storage times, average ammonia emission rates ranged from 0.002 to 0.17 mg NH_3 cm^{-2} h^{-1}, average methane emission rates ranged from 0.001 to 0.15 mg CH_4 cm^{-2} h^{-1} and average carbon dioxide emission rates ranged from 0.21 to 0.76 mg CO_2 cm^{-2} h^{-1}. Nitrous oxide concentrations were very low near detection limit of the instrumentation at 0.67−1.46 mg/m^3 and essentially the same as background levels. Nitrous oxide emission rates remained below 1 µg cm^{-2} h^{-1} regardless of manure amendment type. Hence, N_2O emissions will not be discussed further. Ranges of other gas concentrations at 3 d were 55 to 204 mg/m^3 for NH_3, 8 to 320 mg/m^3 for CH_4 and 1,241 to 3,709 mg/m^3 for CO_2.

3.1 Ammonia

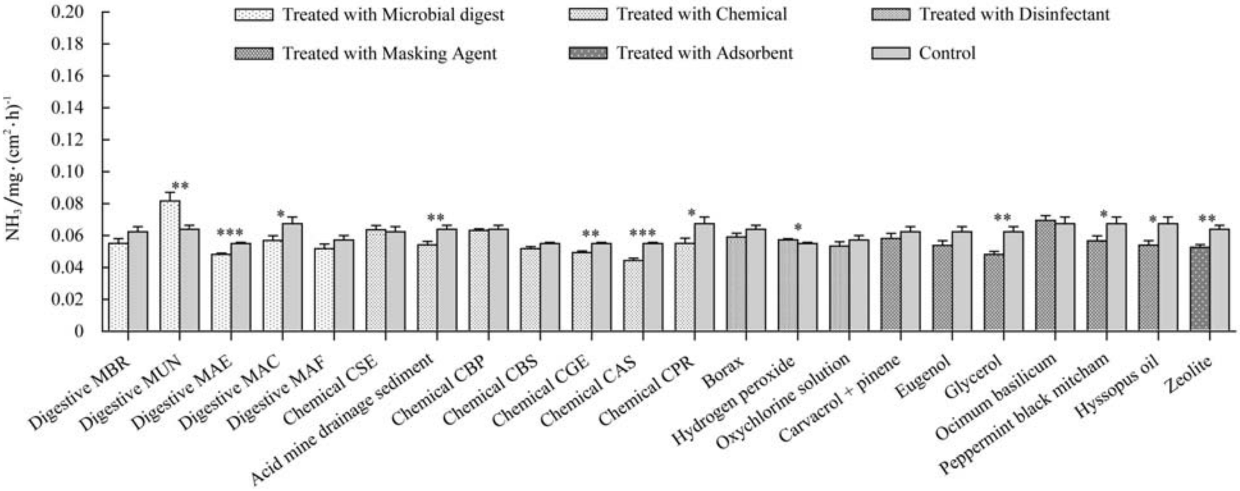
The pH results are very useful in explaining NH_3 emission results (Table 2). After 30 d storage, five of the products caused a clear pH decrease: zeolite (−0.53)< CGE (−0.39)<CBS (−0.35)< MAE (−0.25)< CAS (−0.12). Zeolite showed the biggest pH decrease and reduced NH_3 emissions the most. Six of the products caused a clear pH increase: MUN (+1.49)>Borax (+1.20)>hydrogen peroxide (+ 0.68) > carvacrol (+0.45) > eugenol (+0.29) > glycerol (+0.21). Rather than reducing NH_3 emissions, MUN resulted in a large increase. The probability that a molecule will be protonated or deprotonated depends on the pH of the solution (manure in this case) and the molecule's acid dissociation constant, pKa. The pKa of NH_3 protonation to NH_4^+ is 9.2, which from a practical standpoint refers to the pH at which NH_3 and NH_4^+ are in the same proportion in the solution. Therefore, the lower the pH, the more the equilibrium is shifted to NH_4^+, which will not volatilize from the manure. At pH 8.2, there will be ten times less NH_3 than NH_4^+, at pH 7.2, there will be 100 times less NH_3 than NH_4^+. The cationic form does not escape through volatilization because it is reversibly exchangeable with protons on negatively charged sites on organic particles.

Table 2 Manure slurry pH at the experiment end (30 d) for each amendment1 treatment and control (no amendment). Fresh feces: urine manure slurry pH was 8.30. Manure aged 15 days at 4o C was used at start date 24 January with a pH of 7.83.

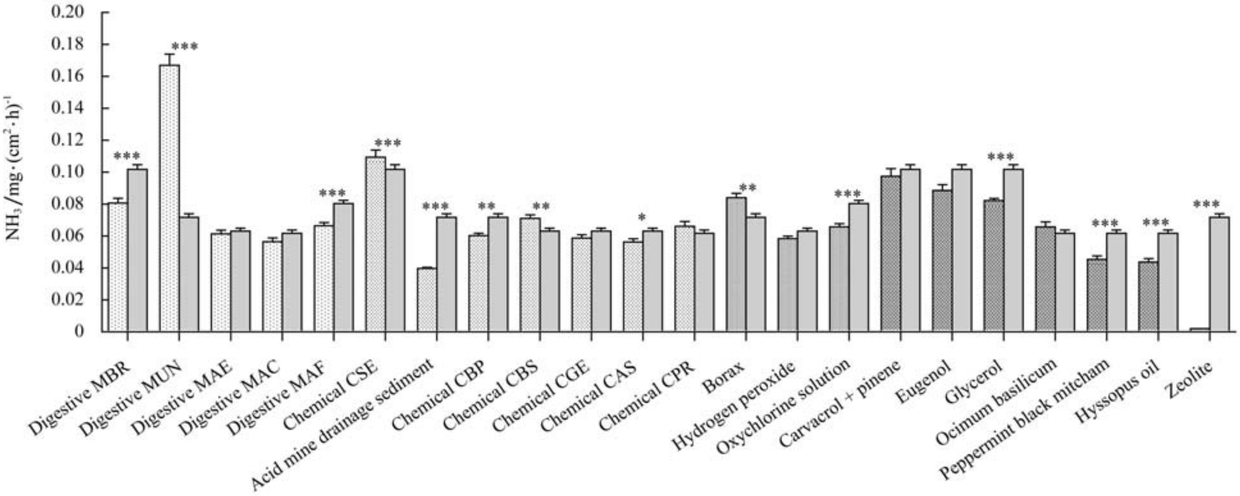
	24-Feb		25-Feb		26-Feb		27-Feb		5-Mar
Control	7.03	Control	6.82	Control	7.30	Control	7.41	Control	7.38
Carvacrol+pinene	7.48	Zeolite	6.29	Hydrogen peroxide	7.98	CPR	7.21	Anthium dioxcide	7.48
Eugenol	7.32	AMD	6.75	MAE	7.05	MAC	7.30	MAF	7.43
CSE	7.03	CBP	6.84	CBS	6.95	Basil oil	7.27		
MBR	6.93	Borax	8.02	CGE	6.91	Peppermint oil	7.18		
Glycerol	7.24	MUN	8.31	CAS	7.18	Hyssopus oil	7.37		

Note: Abbreviations for amendments are found in Table 1.

After 3 d of storage, average NH_3 emission rates were significantly reduced by 11 to 23% (P=0.04 to <0.0001) in ten manure treatments representing four classes of product (Figure 1). Glycerol provided the most reduction in short-term NH_3 emission rates. Glycerol offers a readily available carbon (C) source for microbes that then assimilate ammonium-N into biomass as they utilize the C. The glycerol-amended slurry final pH (30 d) of 7.24 was within the optimal range for microbial growth, further enhancing immobilization of ammonium-N. Anecdotal evaluation of glycerol-amended dairy manure noted a more homogenous slurry and reduction in odor (Mittlelbach, 2009), the latter not substantiated in our screening study (Wheeler et al., 2010a). Perceived odor reduction, in the case of glycerol, perhaps can be partially attributed to the significant reduction of irritating ammonia gas release. Four treatments, AMD and three proprietary chemicals (CGE, CAS and CPR), significantly reduced NH_3 emission as did two essential oils, *Hyssopus* and Peppermint black mitcham, and zeolite. The zeolite sorbed the NH_3 within its structure. The retention of ions and gases on zeolite is influenced by several factors, like size of molecules and cavities, but polarity is very important. Zeolites tend to retain polar adsorbates, such as NH_3. The chemical products may have inhibited the transformation of organic-N into ammonium compounds. The microbial digestive products showed mixed results where two products had no significant effect while two other products (MAC and MAE) produced significant short-term reduction in NH_3 emissions. The digestive product MUN promoted the largest increase in NH_3 emission among all the products tested.



a. 3 d



b. 30 d

Figure 1 Mean ammonia emission rates and standard errors of dairy manure slurry with (treated) and without manure amendments (control) incubated at 20℃ for 3 d (upper) and 30 d (lower). Asterisks above treated bars indicate emission rates were significantly different from control at P=0.05-0.01 (*); 0.01-001 (**); <0.001 (***)

The two treatments that significantly increased NH_3emissions during short-term 3 d storage were hydrogen peroxide and digestive MUN, emitting 4% and 28% more NH_3, respectively, than untreated manure (P=0.035 to 0.005). It is most likely that the addition of digestive MUN to dairy manure increased the production of NH_3 due to the large pH increase (+1.49) that would promote deprotonation of NH_4^+. Hydrogen peroxide also caused a pH increase (+0.68), and may have acted as an antimicrobial during the first 3 days, which would have inhibited N immobilization by the microbial community. Hydrogen peroxide can raise the redox potential and promote aerobic degradation of organic-N, but at high levels it will kill microbes thereby shutting down NH_4^+ consumption.

After 30 d of storage, half of the manure amendments significantly reduced NH_3 emission rates by 11% to 97% (P=0.017 to <0.001) (Figure 1). The greatest reduction of NH_3 emission rates after 30 d were measured in the manure treated with zeolite. Addition of zeolite to dairy manure effectively eliminated NH_3 emission rate because this material reduced pH, served as an adsorbent, and provided a physical barrier to NH_3 gas diffusing from the manure mixture to the headspace above. Bernal and Lopez-Real (1993) reported that zeolites adsorbed aerial NH_3 at a rate of 6 - 14 g/kg of zeolite. Abandoned mine drainage (AMD) was the second most successful amendment in reducing NH_3 emissions by 45% after 30 d storage.

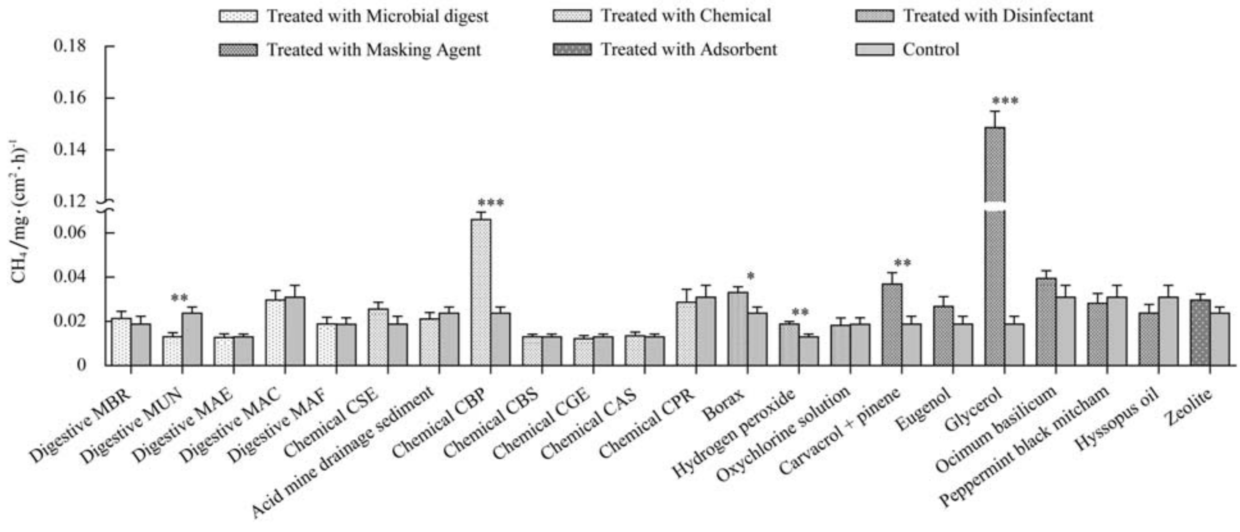
Four amendments, chemicals CSE and CBS, disinfectant borax and digestive MUN, significantly increased emission rates of NH_3 by 13 to 132% after 30 d storage at 20℃ (P=0.009 to <0.001). The large pH increases (>1.0) resulting from the latter two amendments would have promoted NH_3 volatilization. Disinfectant borax may have enhanced NH_3 emission rates by increasing the supply of organic-N from the denatured indigenous microbial community due to its high pH (9.5) and its ability to convert water molecules to hydrogen peroxide (a reaction favored at temperatures warmer than this study) resulting in disinfecting action.

Even though some amendments contained an inorganic-N component mixed in the product, such as digestives MBR, MAE, MAC and MAF, this did not always result in increased NH_3 emission rates after 30 d storage. In fact, digestive MBR significantly decreased NH_3 emission. For these amendments, the amount of N-substrate mixed in the product was insufficient to enhance microbial activity in relation to the N (1.2 Molar mass ammonium-N) already in the manure.

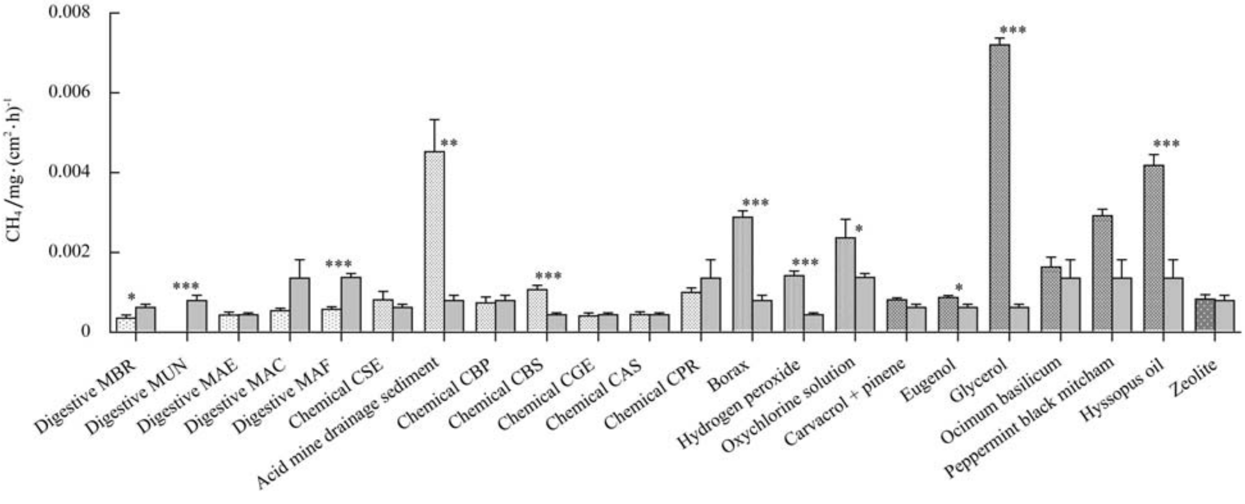
In summary, for both 3 d and 30 d storage periods at 20℃, glycerol, CAS (a proprietary mix of chemical), AMD, *Hyssopus* oil, peppermint oil, and zeolite consistently reduced NH_3 emission rates. A digestive mixture of chemical and surfactants for facultative bacteria, MUN, significantly increased NH_3 emission rates from dairy manure during both short- and medium-term storage. Contradictory results among the various products appeared to be due to differences in pH and whether an amendment inhibited microbial activity by toxicity or provided a substrate (often C source) that microbes used to make biomass, hence, consuming N in the process.

3.2 Methane

Most of the amendments had either no effect or significantly increased CH_4 emissions (Figure 2). Only digestive MUN significantly reduced CH_4 emission rates (46%) in dairy manure (P=0.003 to <0.001) after both storage periods. It is possible that the addition of dispersants and facultative bacterial strains of digestive MUN to the manure slurry inhibited the growth of methanogens through competition for substrates, therefore reducing the potential of CH_4 production. It is not possible to know how the “anaerobic food chain” was affected without knowing redox potential or availability of other electron acceptors like nitrate, ferric iron, or sulfates. These electron acceptors would promote anaerobic respiration and reduce production of the fermentative products that lead to methane production. Another explanation for reduced methane emission would be its consumption at the manure-air interface by methanotrophic bacteria. The digestive amendment MAF significantly reduced CH_4 emissions after 30 d with no effect seen at 3 d. Amendments that acted as antimicrobial agents such as borax, hydrogen peroxide and carvacrol + pinene oils consistently and significantly increased CH_4 emission rates after both 3 and 30 d storage periods (P=0.02 to <0.001). These amendments may have stimulated fermentative activities by manure microorganisms, which would have provided the substrates (acetate, H_2, CO_2) for methanogenesis. In the case of additives such as MBR, repeated aeration caused by weekly mixing (Table 1) of treated manures could have inhibited methanogenesis during the 30 d period. Overall, CH_4 emission rates after 30 d were all very low compared to 3 d with most products 10-times less but ranging from 4 to 66 times lower after a month of storage at 20℃.



a. 3 d



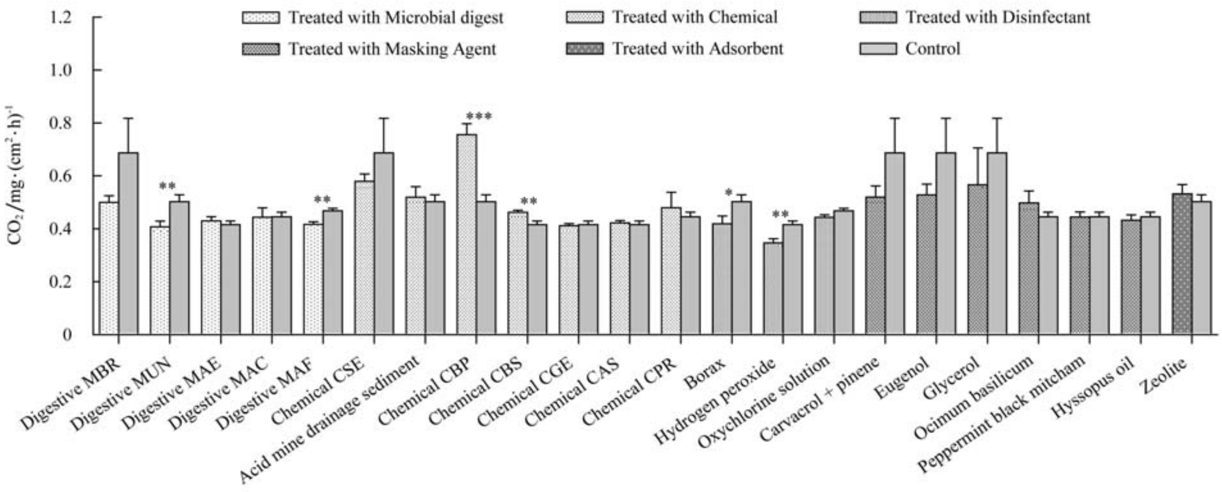
b. 30 d

Figure 2 Mean methane emission rates and standard errors of dairy manure slurry with (treated) and without manure amendments (control) incubated at 20℃ for 3 d (upper) and 30 d (lower) [Note the large change in y-axis scale of the two sub-graphs]. Asterisks above treated bars indicate emission rates were significantly different from control at P=0.05-0.01 (*); 0.01-001 (**); <0.001 (***)

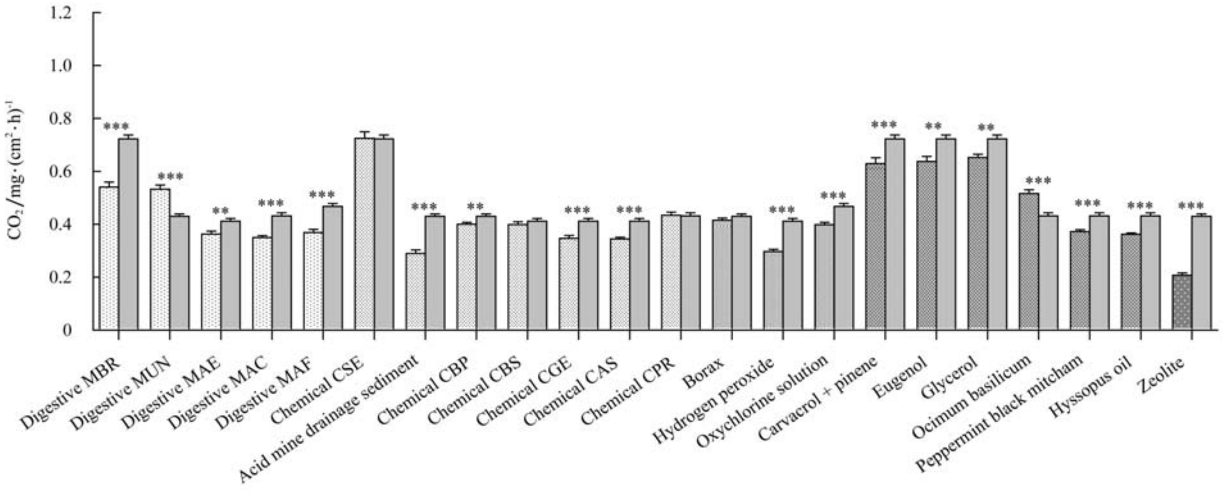
Amendments that were effective at NH_3 control often had poor results for CH_4 reduction. Glycerol effectively reduced NH_3 for both storage periods yet resulted in greatly increased CH_4 emissions for both storage periods, possibly through enhanced production of substrates for methanogenesis. Zeolite showed no significant change in CH_4 emissions at either storage period likely due to CH_4 being a non-polar molecule, hence, not retained by the zeolite structure. The AMD treatment was the most consistent in reducing NH_3 at both 3 and 30 d yet was not effective in reducing CH_4 emissions. AMD provided no significant methane control at 3 d and, showed the greatest increase in CH_4 emissions at 30 d (although the scale of this emission was much reduced versus the rate recorded at 3 d). While MUN significantly increased NH_3 emissions it was the most effective at CH_4 control (discussed above). The six masking agents all appeared to increase CH_4 emissions at 30 d, but only three were statistically significant.

3.3 Carbon Dioxide

Changes in GHG CO_2 emissions during study conditions were not as dramatic as those observed for CH_4 emissions. Average CO_2 emission rates were significantly reduced after short-term storage by 11% to 19% following the addition of four amendments: digestive MUN and MAF, borax and hydrogen peroxide (P=0.04−0.001) (Figure 3). However, after long-term storage, most (18 out of 22) amendments showed significant reduction of CO_2 emission rates in dairy manure versus control manure with the reduction ranging between 12% and 52% (P=0.01−<0.0001). Zeolite had the greatest reduction of about half the emission at 30 d. Carbon dioxide is strongly adsorbed on zeolite, while CH_4 is not, to the extent that zeolite is used in mixtures to separate these two compounds. Average CO_2 emission rate for all products was <0.58 mg CO_2 cm^{-2} hr^{-1} after a month of storage. Significant increases in CO_2 emissions were observed in manure treated with proprietary chemicals CBS and CBP after 3 d storage and manure treated with the masking agent *Ocimum basilicum* (basil) oil and digestive MUN after 30 d storage (P=0.01−<0.0001). In all treated and untreated manure, average CO_2 emission rates were 0.8 to 2.6 times lower than 3 d emission rates after a month of storage. For both CH_4 and CO_2 emission rates, it appears that aging the manure slurry for 30 d at 20℃ significantly reduced gas production by 11 to 100% (P=0.05 −<0.0001).



a. 3 d



b. 30 d

Figure 3 Mean carbon dioxide emission rates and standard errors of dairy manure slurry with (treated) and without manure amendments (control) incubated at 20℃ for 3 d (upper) and 30 d (lower). Asterisks above treated bars indicate emission rates were significantly different from control at *P*=0.05-0.01 (*); 0.01-001 (**); <0.001 (***)

4 Conclusions

Efficacy in reducing gas emission rates from dairy manure using the 22 amendments having five different modes of action varied with respect to duration of storage and target gas. None of the amendments showed significant reduction of both NH_3 and GHG after both short- and long-term storage periods ($P<0.05$) at 20℃. After 3 d storage at 20℃, NH_3 emission rates were reduced by 11 to 23% in ten manure treatments representing all classes of product except disinfectant. Meanwhile only six amendments that acted as oxidizing agents, masking agents or adsorbent significantly reduced NH_3 by>10% (*P* 0.04 to<0.0001) after both 3 and 30 d storage. The addition of microbial digestive MUN or glycerol to dairy manure showed the complexity of controlling emissions of both NH_3 and GHG during storage. Following MUN application, significant decreases of CH_4 gas were associated with the greatest significant increases of NH_3 gas during both storage periods. Meanwhile, NH_3 emission rates decreased and CH_4 emission increased in response to glycerol treatment for both short- and long-term storage.

Since significant reductions of GHG (CH_4 and CO_2) emission rates were observed in some treated and all untreated manure samples after 30 d storage period, the efficacy to control these gases in response to amendment treatments may have been due to the combined effects of pH, aging and active ingredients of some of the products. In response to prolonged storage time of 30 d, some amendments increased NH_3 emission rates, specifically those that showed substantial pH increases. Some products added N material yet the concentration of ammonium-N (>1M) in the manure itself is so high that N added from products would be unlikely to have an impact. Manure also has high availability of organic N.

Based on our study, amendments that have potential to reduce NH_3 and CO_2 emission rates 10 to 44% in dairy manure after 30 d storage of manure were the abandoned mine drainage (AMD), clinoptilolite zeolite, masking agents *Hyssopus*, eugenol, and peppermint oils, disinfectant anthium dioxide and a digestive aerobic/facultative microbes (MAF). While reductions of gas emission rates following the addition of 22 amendments varied after short- and long-term storage at 20℃, our results show that the efficacy of these products to control gas emissions in dairy manure is likely limited to the amount of active ingredient applied. It is difficult to systematically discuss the many simultaneous processes involved in gas reduction given the variety (and unknown nature) of some of the amendments. This screening trial offers insight into magnitudes of gas emissions along with reflections on how modes of action can influence simultaneous changes among selected gas emissions. With only one sample per amendment caution is advised, as replicated study of the promising amendments can better determine the variation in treatment efficacies.

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References

Agle, M., A. N. Hristov, S. Zaman, C. Schneider, P. Ndegwa, and V. K. Vaddella. 2010. The effects of ruminally degraded protein on rumen fermentation and ammonia losses from manure in dairy cows. J. Dairy Sci, 93: 1625–1637.

Amon, M., M. Dobeic, R. W. Sneath, V. R. Phillips, T. H. Misselbrook, and B. F. Pain. 1997. A farm-scale study on the use of clinoptilolite zeolite and De-Odorase (R) for reducing odour and ammonia emissions from broiler houses. Bioresource Technology, 61: 229–237.

ASTM E1755 (2001. R2007) Standard Test Method for Ash in Biomass. ASTM International, West Conshohocken, PA.

ASTM E1756. 2008. Standard Test Method for Determination of Total solids in Biomass. ASTM International, West Conshohocken, PA.

Bernal, M. P., and J. M. Lopez-Real. 1993. Natural zeolites and sepiolite as ammonium and ammonia adsorbent materials. Biores. Technol, 43: 27–33.

Calsamiglia, S., M. Busquet, P. W. Cardozo, L. Castillejos, and A. Ferret. 2007. Invited review: Essential oils as modifiers of rumen microbial fermentation. J. Dairy Sci, 90(6): 2580–95.

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.

Clanton, C. J., R. E. Nicolai, and D. R. Schmidt. 1999. Chemical additions to swine manure to reduce hydrogen sulfide losses: a laboratory study. ASAE paper No.994007. St. Joseph, MI.

Cai, L., J. A. Koziel, Y. Liang, A. T. Nguyen, and H. Xin. 2007. Evaluation of zeolite for control of odorants emissions from simulated poultry manure storage. J. Environ. Qual, 36: 184–193.

Cole, C. A., H. D. Bartlett, D. H. Buckner, and D. E. Younkin. 1976. Efficacy of certain chemical and biological compounds for control of odor from anaerobic liquid swine manure. J. Animal Sci., 42: 1–7.

Heber, A. J., J. Ni, A. L. Sutton, J. A. Patterson, K. J. Fakhoury, D. T. Kelly, 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 p.

Jelínek, A., M. Dědina, P. Plíva, and J. Souček. 2004. Research of biological agents effects on reduction of ammonia concentration in stables of intensive farm animals breeding. Res. Agric. Eng., 50: 43–53.

Lee, S., J. K. Han, Y. J. Choi, and K. Nam. 2007. Reduction of ammonia and hydrogen sulfide emission from swine manure using aqueous foams amended with microorganisms and chemical additives. Clean, 35(3): 230–234.

Massé, D. I., J. Lavoie, G. Barnet, F. Croteau, E. Topp, and L. Massé. 2004. The development of experimental procedures for the evaluation of additives to attenuate manure odour, and the impact of these additives on workers, animals and the environment. Water Sci. and Technology, 50(4): 257–265.

McCrory, D. F., and P. J. Hobbs. 2001. Additives to reduce ammonia and odor emissions from livestock wastes: a review. J. Environ. Qual., 30: 345–355.

Mittelbach, M. 2009. Personal communication. Institute for Chemistry, Dept. of Renewable Resources. Karl-Franzens University Graz, Austria.

Morse, D., R. A. Nordstedt, H. H. Head, and H. H. Van Horn. 1994. Production and characteristics of manure from lactating dairy cows in Florida. Trans. ASAE, 37(1): 275–279.

MWPS. 2008. Mitigating air emissions from animal feeding operations. Conference Proceedings: MWPS-AIR. MidWest Plan Service. Iowa State University, Ames, IA. 306 pages.

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

Tada, C., Y. Yang, T. Hanaoka, A. Sonoda, K. Ooi, and S. Sawayana. 2005. Effect of natural zeolite on methane production of anaerobic digestion of ammonium rich organic sludge. Biores. Tech., 96: 459–464.

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

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, ASABE, St. Joseph, MI.

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, V. A. Ishler, and M. A. Bruns. 2010a. Amendments for mitigation of odor emissions from dairy manure: Preliminary screening. ASABE Paper No. 1008658. ASABE, St. Joseph, MI.

Wheeler, E. F., M. A. A. Adviento-Borbe, R. C. Brandt, M. A. Bruns, P. A. Topper, H. A. Elliott, A. N. Hristov, V. A. Ishler, D. A. Topper, R. E. Graves, R. S. Thomas, and G. A. Varga. 2010b. Dairy manure amendment effects on odor and gas emissions. Paper No. CSBE10644. XVIIth World Congress of the International Commission of Agricultural Engineering (CIGR), Quebec City, Canada.

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, V. A. Ishler, and M. A. Bruns. 2011. Tentative-in second review. Evaluation of odor emissions from amended dairy manure: preliminary screening. Agricultural Engineering International CIGR Ejournal.