Evaluation of Odor Emissions from Amended Dairy Manure: Preliminary Screening

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ABSTRACT

Manure amendments have shown variable effectiveness in reducing odor. Twenty-two amendments were applied to dairy manure then evaluated for odor reduction efficacy after storage at 20°C for 3 d and 30 d. Amendments represented differing primary modes of action including: microbial digestive, oxidizing, disinfecting, masking, and adsorbent. Each amendment was added to 2 kg dairy manure (1:1.7 urine:feces; 12% total solids) following recommended rates. In this preliminary screening, one sample (n=1) of each amendment was evaluated along with untreated manure (Control). Odor emission from each treated manure and Control was estimated twice by five or six qualified odor assessors (n=10 or 12) after each storage duration, using an international standard for triangular forced-choice olfactometry. Odor quality was defined using hedonic tone, Labeled Magnitude Scale and ASTM methods for supra-threshold odor intensity, and an odor character wheel for descriptors. For selected treatments, odor emissions were significantly reduced relative to Control at 30 d versus 3 d incubation (P<0.0001). However, no amendment was significantly effective for both incubation times. Likewise, for all amendments tested, aging the manure slurry for 30 d significantly reduced odor emission and odor intensity (P<0.0001). A proprietary microbial amendment (Alken Enz-Odor + Clear Flo: aerobic/ facultative microbes with growth factors), disinfectant (hydrogen peroxide), and masking agent (*Hyssopus officinalis* essential oil) provided significant short-term control of odor (P <0.06). However, after 30 d seven amendments significantly increased odor emission (P<0.02) while only two amendments offered a significant efficacy (P<0.0001): a proprietary microbial aerobic/facultative product (Bio-Regen) and a proprietary mix of chemicals (Greaseater), both with weekly re-application. Hedonic tone observations suggested an improvement to "slightly to moderately unpleasant" smell versus untreated manure for all amendments except clinoptilolite

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zeolite adsorbent. Hedonic tone improvement was correlated with reduced manure odor supra-threshold intensity.

Keywords: Odor, hedonic tone, odor strength, amendments, additives, dairy manure, United States of America

1. INTRODUCTION

Manure handling and storage facilities can be a source of malodors in dairy operations. Offensive odor is partly the result of incomplete anaerobic decomposition of stored manure. Studies have identified 35 to 73 volatile compounds in dairy manure (Filipy et al., 2006, Rabaud et al., 2003, Sunesson et al., 2001) with the most important odorous manure components found to be the volatile fatty acids (VFA), *p*-cresol, indole, skatole, along with hydrogen sulfide (H_2S) and ammonia (NH_3) by virtue of either their high concentrations or low odor thresholds (O'Neil and Phillips, 1992). Wright et al. (2004) has identified *p*-cresol, *p*-ethyl phenol and isovaleric acid as the most persistent and biggest contributors to odor downwind of the source. Miller and Varel (2001) determined that low starch content of beef cattle feedlot manure limited VFA production. They noted in laboratory studies that ethanol, acetate, propionate, butyrate, lactate and hydrogen were the major fermentation products of stored cattle manure. Due to far-reaching environmental and socioeconomic concerns, efforts to reduce odor, NH_3, H_2S, and greenhouse gas emissions from animal agriculture are essential.

In recent years, many treatments such as biogas production, anaerobic or aerobic waste treatment, and solids separation have been available to farmers for managing livestock odor and manure wastes. While these methods have proven effective, their use may be limited by cost and/or operational expertise requirements.

One treatment approach that appears practical and economical to farmers is the use of livestock manure amendments. Numerous types of amendments have been proposed to reduce odor and gas emissions. McCroy and Hobbs (2001) categorized commercial additives according to their modes of action: (1) digestive additives; (2) disinfecting additives; (3) oxidizing agents; (4) adsorbents, and (5) masking agents. Chemical pH adjustment additives are also used to manage off-gas emissions. Notably, in a study of 35 swine manure products (n=3), Heber et al. (2001) found that none of the additives significantly (α=0.05) reduced odor emission (dilution threshold) after 42 d of incubation at 20^{o}C. In an evaluation of simulated cattle manure, Perschbacher-Buser et al. (2005) evaluated five commercial odor control additives. They found higher odor emission rates and lower hedonic tone (more unpleasant) than control samples at 9 d and 144 d incubation periods, concluding that these products were not effective. Despite the inconsistent performance of commercial manure amendments, these products continue to be the most widely available and popular type of odor control.

Microbial digestive additives consist of selected microbial strains and/or enzymes that reduce production or enhance decomposition of odorous compounds in animal wastes. Several studies have attempted to identify bacteria and the pathways that produce odors (Mackie et al., 1998, Zhu and Jacobson, 1999). Zhu and Jacobson (1999) found that the most important genera for odor production were *Eubacterium* and *Clostridium*. All studies conclude that more research is required before these pathways can be fully understood. Ritter (1989) reported that the efficacy of digestive additives was due to the elimination of only selected odorants. Controlling specific odorants cannot guarantee a reduction in the perceived malodor from manure, as no consistent correlation between specific odorants and nuisance conditions has been identified. Nevertheless, digestive additives are the most popular of the proprietary compounds sold for odor control.

Disinfectants reduce the formation of odorants by inhibiting microbial mediated processes occurring in the manure. Varel and Miller (2000) found an 80% reduction of fermentation gas and 50% reduction of volatile fatty acids when cattle manure was treated with chlorhexidine diacetate (2 mM), iodoacetate (2 mM), and α-pinene (3.8 mM) during a 30 d incubation period. Amon et al. (1997) found no statistically significant reduction in the odor concentration or odor emission rate when De-Odorase® additive (extract of *Yucca shidigera*) was sprayed on poultry litter. Although disinfectants can produce a short-term reduction in emissions, toxicity and cost concerns have limited their use. More recently, selected essential oils are being promoted as effective and safe antimicrobial or antiviral (disinfectant) agents that also act as masking agents in the control of odor. Essential oils are aromatic oily liquids extracted from plant material via expression, fermentation, or distillation methods (Burt, 2004) and are known to have various modes of action.

Oxidizing agents transform odorous compounds into less offensive gases by chemical oxidation. Strong oxidizing agents act as disinfectants through their ability to degrade enzymatic proteins and oxidize sulfides, mercaptans, and NH_3. In a study of ferric chloride ($FeCl_3$) on degradation of odorous compounds, Castillo-Gonzalez and Bruns (2005) reported a significant reduction of volatile fatty acids concentration (propionic butyric, isobutyric, valeric and isovaleric) in swine manure between 2 and 6 d incubation at 25°C. At concentrations of 480 and 240 mg $L^{-1}$of potassium permanganate ($KMnO_4$), Ritter et al. (1975) reported that the mixture was effective in controlling odors from dairy slurry. In a laboratory study, hydrogen peroxide (H_2O_2) caused a very significant reduction in p-cresol levels (Eniola et al., 2006). Govere et al. (2007) found complete removal of three phenolic odorants, without recurrance for 72 hr, from swine waste via gas chromatograph analysis after the addition of a mixture of hydrogen peroxide and miniced horseradish while odor intensity was cut in half as determined by a human odor panel. One disadvantage of using H_2O_2 as an amendment is that solutions >8% are corrosive. Generally, oxidizing agents are effective in reducing malodors, but only for a short period, due to the large quantities of reagents required for complete oxidation.

Natural zeolite, clinoptilolite (an ammonium-selective zeolite), has been shown to enhance adsorption of volatile organic compounds 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. Studies conducted by Amon et al. (1997) showed no statistical reduction in odor concentration or odor emission rate for clinoptilolite treated poultry manure as compared to control. Similarly, Miner and Stroh (1976) found zeolite ineffective in reducing odor intensity from a cattle feedlot. It is believed that the frequent poor performance of absorbents stems from selective odorant adsorption, leaving other noxious odors to escape.

Amendment of manure with alkaline materials such as cement kiln dust, lime, or other alkaline by-products can increase the pH to above 12.0, which limits the vast majority of microbial activity, including odor producing microorganisms (Veenhuizen and Qi, 1993, Li et al., 1998). In a swine manure storage pit field study, addition of an alkaline by-product containing 46% lime (CaO), 23.8% silica (SiO_2), 4.5 % ferric oxide (Fe_2O_3), and aluminum (Al_2O_3), odor concentration was significantly reduced.

An effective odor amendment must be inexpensive, efficient and suitable to dairy farm management. Several of these amendments 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. disinfecting or alkaline materials). Extra benefits of an effective odor amendment may offer farmers, in addition to odor and gas emission controls, improved manure handling properties, reduction in surface water pollution and in some cases reduction in the levels of pathogenic bacteria with potential benefit in soil pH adjustment.

1.1 Study Objectives

This study focused on assessment of the efficacy of manure amendments with reported ability to reduce odor emissions in dairy manure storage. The objective of this study was to evaluate performance of 22 manure amendments in reducing odor emissions from dairy manure after short term (3 d) and medium term (30 d) storage at 20^oC. This study served as a screening of 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 also conducted on gas emissions from these manure amendments and reported elsewhere (Wheeler et al., 2010a; 2011).

2. MATERIALS and METHODS

2.1 Manure Amendments

This screening study evaluated twenty-two manure amendments with selection based on claims or reports that they reduced dairy manure odor. Eight amendments were commercially-available products where active ingredient levels were not necessarily revealed. Several common compounds, abandoned (a.k.a. acid) mine drainage sediments, hydrogen peroxide, glycerol, and selected essential oils, were evaluated based on anecdotal claims for their odor (or gas) reduction performance. In total, the materials comprised five different classes of product that included seven microbial additives, six oxidizing agents/chemicals, three disinfectants, six masking agents, and an adsorbent. Table 1 summarizes the products tested and the corresponding rates and methods of application for stored dairy manure. Manufacturers of proprietary compounds were contacted for a recommended rate of application based on conditions specified for this study. This experiment did not attempt to fully simulate manure storage conditions involving continual addition of fresh manure to storage vessels. Application rates for non-commercial compounds were based on researcher determinations.

Table 1. Description of twenty-two manure amendments used in the dairy manure odor (and gas) 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	40mL 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	20g 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)

[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 x H_2Sppm x 10,000 m^3d^{-1} 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 10g Fe per 1% solid content.
[6]Hydrogen peroxide rate determined from Clanton et al. (1999) lab H_2S reductions.
[7]Anthium dioxcide at 40 ppm achieved within slurry

2.2 Manure Preparation

Manure was collected separately as urine and feces from 8 to 10 lactating dairy cows on the control diet of a feed additive experiment conducted at the Dairy Production Research and Teaching facility at the University Park campus of Pennsylvania State University (PSU). Manure slurry was prepared as 1:1.7 urine to feces ratio (12.1% total solids; pH 8.3) and stored at 4^{o}C for 15 d to produce an "aged" stable feedstock material. There was no bedding or feed/water incorporated into the manure samples as would be found in manure typically stored at a dairy farm. A 500 g subsample from the prepared manure slurry was sent to the PSU Agricultural Analytical Services Laboratory for standard analysis. On a dry weight basis the fresh manure contained 49.8 and 19.1 g kg^{-1} total N and NH_4-N, respectively. After aging the manure pH was 7.83 while total N, NH_4-N and organic N on a dry weight manure basis was 48.9, 24.1 and 24.8 g kg^{-1}, respectively. Manure feedstock after aging had 12.1% total solids using oven drying standard-methods [ASTM 2008].

2.3 Laboratory Storage 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 (Table 1). These jars also served as the flux chamber vessel for odor/gas sample collection (Section 2.4). For this preliminary screening of amendments, only one sample of each amendment was prepared (n=1) to have an affordable (reduced odor panel expense) prescreening of many amendments versus replicated screening of a few amendments. Jars were incubated in a walk-in, temperature-controlled storage chamber for 3 d and 30 d at 20^{o}C. While 20^{o}C coincides with many other studies of manure amendments, it is considered a warmer temperature than experienced by manure storages in the northeastern USA. Untreated manure Controls were prepared and incubated in a manner identical to treated samples. The jars were loosely sealed to avoid over pressurization during incubation. Due to logistical and resource constraints associated with odor panel assessments, treatments were prepared in five batches, which included Control (untreated) manure in each batch. It was important to include untreated manure in each batch since even with the "aged" manure feedstock there was significant variation of Control manure emissions found during preliminary trials. Amendments representing the various classes of product were randomly spread over the five batches to avoid bias. Batches were evaluated on sequential days using the same odor assessors (in most cases). Although each amendment had one sample prepared, statistical analysis (section 2.6) evaluated 10 to 12 independent assessments of each sample at 3 d and again at 30 d storage.

2.4 Odor Emission Measurement and Calculation

The treated and Control jars were removed from the temperature-controlled storage and placed in a multi-chamber steady-state gas emission detection system (Wheeler et al., 2007. Wheeler et al., 2010a). Briefly, this instrumentation system had eight identical flux chambers constructed of 3.8 L glass jars with Teflon™-lined lids integrating an inlet air distribution ring (these were the same glass jars in which the samples were stored). Each chamber had calibrated flow-metered sweep air and sampling sequence controlled via relay and solenoid valve (to analyzer or exhaust) commanded from customized LabVIEW™ computer software (National Instruments, Austin, TX). Each flux chamber jar was partially immersed in a 20^{o}C water bath and supplied with a continuous 2 L min^{-1} filtered, humidified sweep air. Two of the eight flux chamber jars contained distilled water as "blanks" to check for cross-contamination of sampling lines and for determining background odor concentrations.

Two to 3 h after manure placement in the gas measurement system, approximately 7.0 L of odorous headspace gas was collected for olfactory evaluations from each of the chambers (at solenoid vent) in 10 L preconditioned Tedlar™ bags. All odor samples were presented to trained panelists and analyzed for detection threshold (DT) and recognition threshold (RT) levels using an olfactometer (Ac'Scent International, St. Croix Sensory, Lake Elmo, MN) following the Triangular Forced-Choice method (CEN, 2003). Five panelists (minimum) conducted evaluations of 6 manure samples (5 amended manure treatments plus one Control untreated sample), and a distilled water blank sample. All samples were evaluated twice each. Thus, each individual sample was subjected to at least ten independent evaluations at both 3 d and 30 d. All odor panel emission and qualitative evaluations were performed within 7 h of sample collection.

Odor emission was computed using Eq. 1:

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

Where, E is manure odor emission rate (OU cm^{-2} min^{-1}), C_1 is odor concentration of manure (OU m^{-3}), C_{BLK} is odor concentration of water blanks (OU m^{-3}), Q is flow rate of filtered air supplied through each chamber (0.002 m^3 min^{-1}), and A is the surface area of manure in each chamber (cm^2). The odor emission rate (OU cm^{-2} hr^{-1}) was adjusted by converting emission rates in minutes to hour.

In order to account for the differing sensitivity of qualified assessors, the 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 the 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 the odor detection threshold of the n-butanol standard (OU m^{-3}).

2.5 Odor Quality

After use in the olfactometer, the bag containing the odorous (or blank) gas sample was moved to a different laboratory where each panelist would smell the undiluted bag contents and evaluate qualitative measures of hedonic tone, character, and intensity. Each sample was evaluated six independent times for each storage period. Hedonic tone (pleasantness) was subjectively quantified using the scale shown in Figure 1 (-11 for extremely unpleasant to +11 for extremely pleasant). Odor character was determined with a word-descriptive wheel shown in Figure 2.

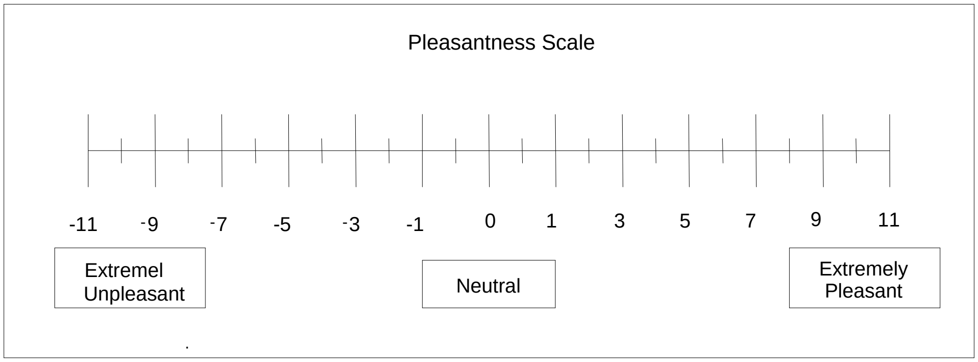

Figure 1. Assessors noted the subjective pleasantness (hedonic tone) using this 22-unit scale, without the quantifying numbers, for each sample.

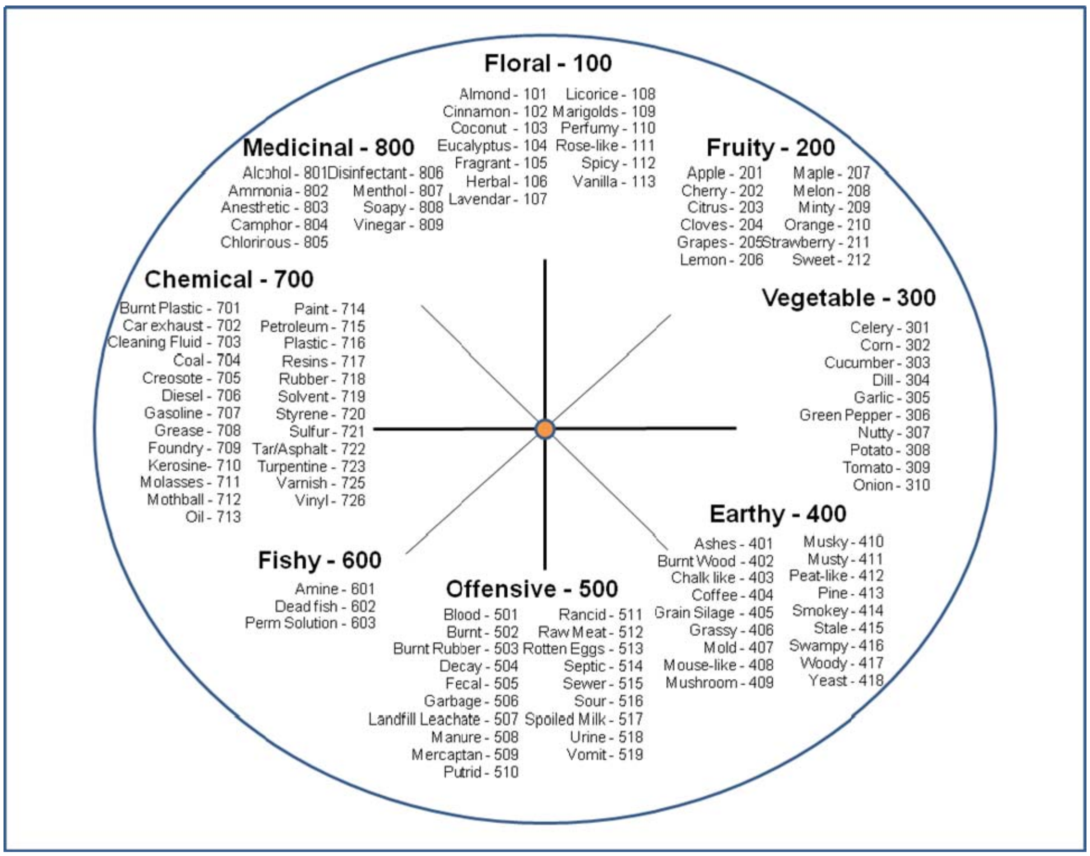

Figure 2. Character wheel used by assessors to describe, via words, supra-threshold odor character during qualitative evaluations (St. Croix Sensory, 2003).

The panelists assessed the odor intensity using both the Labeled Magnitude Scale method (LMS, Fig. 3), a non-linear scale ranging from 0 to 100 (Green et al., 1996), and the ASTM method for referencing supra-threshold odor intensity (ASTM E544-99, 2004). For the ASTM odor intensity reference scale (OIRS) method a series of concentrations of n-butanol in water were prepared as the reference for comparison to odor intensities of the odor samples. In accordance with the static scale OIRS method, n-butanol concentrations represent a geometric progression, with a scaling factor of three. The concentrations used in this study were 0, 250, 750, 2250, 6750 and 20,250 ppm and assigned odor intensity levels of 0, 1, 2, 3, 4 and 5, respectively (Fig. 4). All assessments were performed at room temperature (~23^{o}C). When an assessor selected an intermediate OIRS level (e.g. 2.5), the geometric mean of adjacent lower and higher n-butanol concentrations was assigned. The 0.5 OIRS level was set equivalent to 83.3 ppm n-butanol in water (1/3 of level 1 at 250 ppm), consistent with the 3x scaling factor. All OIRS data were evaluated using log 10 transformation to determine the best estimate supra-threshold mean and standard deviation. To assist reader interpretation, mean log 10 n-butanol concentration determined by the panel was transformed into arithmetic values for presentation herein.

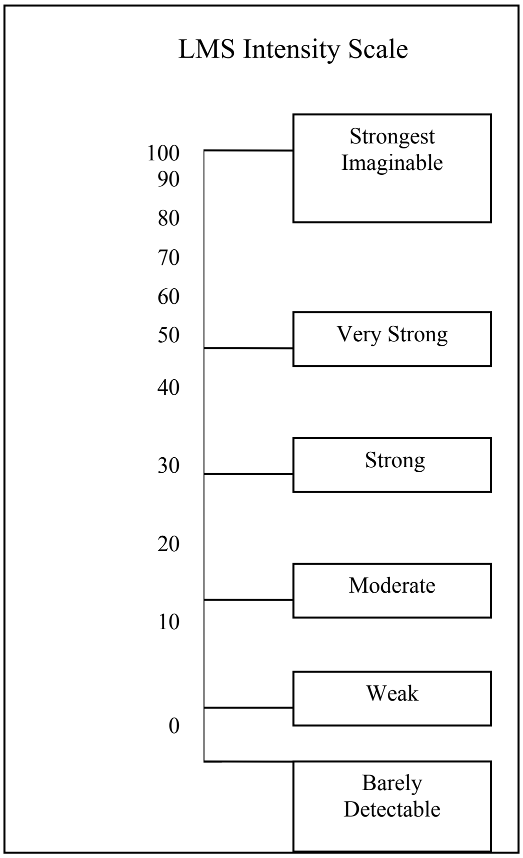

Figure 3. Labeled magnitude scale (LMS) for odor intensity where odor assessor marks the scale on left near or between descriptive term(s) that represents the sample. The numerical values are not included on the panelist assessment sheets. After assessment the researcher processes the responses by assigning appropriate numerical scores to allow quantification (Green et al., 1996).

Odor Intensity via OIRS Method (circle desired response)	
5+	
5.0	Strongest
4.5	↑
4.0	
3.5	
3.0	
2.5	
2.0	
1.5	
1.0	
0.5	
0.0	Odorless

Figure 4. Scale used for ASTM E544-99 (2004) Odor Intensity Referencing Scale Method (OIRS) in combination with known concentrations of five reference odor intensities as n-butanol in water at room temperature.

2.6 Statistical Analysis

Odor emission rates at 3 d and 30 d of treated and untreated manures samples were plotted into linear regression where slopes and intercepts were compared using the P-value test (*P*-value<0.05) (SAS, 2003). When the P-value test showed that there was a difference between a treated odor emission from its control manure sample, a percent change in odor emission was calculated. Odor quality measures were analyzed using basic statistics. Relationships of odor hedonic tone, intensity and emission rates were assessed using Pearson correlation.

3. RESULTS and DISCUSSION

3.1 Odor Emission

Odor emissions after 3 d were significantly higher than emissions after 30 d storage at 20^{o}C in all manure treatments ($P \leq 0.0001$; Fig. 5). For both incubation periods, odor emission rates ranged from 0.52 to 3.91 OU_E cm^{-2} hr^{-1} with the highest emission measured in treatments using aerobic/facultative microbial (MAE) and eugenol, both at 3 d, and lowest in manure treated with abandoned mine drainage and oxychlorine (a.k.a. anthium dioxcide), both at 30 d. None of the 22 manure amendments significantly reduced odor emissions from dairy manure for both 3 d and 30 d incubation, although some amendments showed promising results at one or the other storage period. Statistically significant changes in odor emission were found once treated manure differed from the Control manure by at least 25-35%.

Three products showed significant short-term odor control at 3 d. One successful amendment was a microbial digest/enzyme (MAF showing a 33% reduction in odor), another a disinfectant (hydrogen peroxide with a 45% reduction) and the third a masking agent (*Hyssopus officinalis*) essential oil with a 27% reduction (P= 0.04, 0.03, 0.056 respectively). These products offer potential for use prior to the transition from storage to land application by providing short-term odor reduction.

After 3 d incubation at 20^{o}C, the highest significant odor reduction (45%) was measured in manure treated with hydrogen peroxide. Hydrogen peroxide reduced odor, presumably through reaction with H_2S to produce elemental sulfur and water under pH <8.5 (EPA, 1985). Borax did not reduce odor, even though its mode of action in aqueous solution involves conversion of water molecules to hydrogen peroxide. This later reaction is favored under hot conditions (60^{o}C), thus it may not have been a dominant mechanism at this 20^{o}C temperature evaluation. Borax also has a high pH (9.5) so the boron salts inhibit metabolic processes of many organisms. Reductions of odor emission by 22 or 17%, respectively, were measured in peppermint oil and basil oil (*Ocimum bacillicum)* treated manure but the reduction was not significant (*P* = 0.12-0.22). Zeolite provided a slight (11%) but non-significant reduction in odor at 3 d.

It appears that the scent emitted by naturally aromatic materials contributed to an increase in odor detection/recognition perceived by assessors. The addition of aromatic materials eugenol, oxychlorine solution, and carvacrol +pinene to dairy manure increased odor emission by 75, 24 and 27%, respectively, after 3 d incubation although only eugenol was statistically significant (P= 0.01). Our results differed from the findings of Varel and Miller (2000) and Varel et al. (2007) on the use of carvacrol + pinene in dairy manure odor control. Their studies found a reduction of odor emission from stored cattle manure (30-60 d). Perhaps the increase in odor emission in our study was due to differences in product application rate, sample volume, ratio of urine to feces or incubation period. Pinene is only a masking agent, but in combination with carvacrol (and thymol) the mixture was found to reduce anaerobic bacteria in manure within 2 d (Varel, 2002).

Manure treated with the relatively odorless glycerol, a byproduct of biodiesel production, also increased odor emission 27% (although not significant P=0.19) after 3 d of incubation at 20^{o}C. This is contrary to anecdotal reports (Mittelbach, 2009) of odor reduction and more homogenous manure after its addition to manure storage. Mittelbach (2009) notes that glycerol contains methanol, which is toxic and explosive, so use in enclosed manure pits is discouraged. The effect of glycerol (glycerine*;* glycerin*;* glycerol*;* polyhydric alcohol) on odor production in dairy manure is unclear without chemical analysis. However, it is notable that glycerol is a larger molecule than water and when mixed in manure slurry may decrease the activity of water by excluding water molecules from other molecules.

For all products tested, it appears that aging the manure slurry for 30 d at 20^{o}C reduced malodor gas production and odor strength by 10 to 105% (*P* = <0.0001) compared to emissions at 3 d. Odor emission rates ranged between 0.56 and 2.75 OU_E cm^{-2} hr^{-1} after 30 d of incubation. Odor emission rates were significantly reduced by 48% following the addition of digestive aerobic/facultative MBR and chemical (CGE), in part, as a result of frequent re-application to dairy manure (Fig. 5 and Table 1). After 30 d incubation, some amendments, regardless of the class of product, significantly increased odor emissions compared to Control by 46 to 177% at 20^{o}C (Fig. 5) indicating that none of the five product classifications consistently reduced odor after storage at warm temperature. In contrast to its performance at 3 d storage, hydrogen peroxide significantly increased odor emission 46% (P=0.01) after 30 d. Zeolite had the highest increased odor emission of 177% (P=0.0008) after 30 d as did chemicals CPR at 89% and borax at 148% and essential oil *Ocimum basilicum* at 89% (all at P<0.0001).

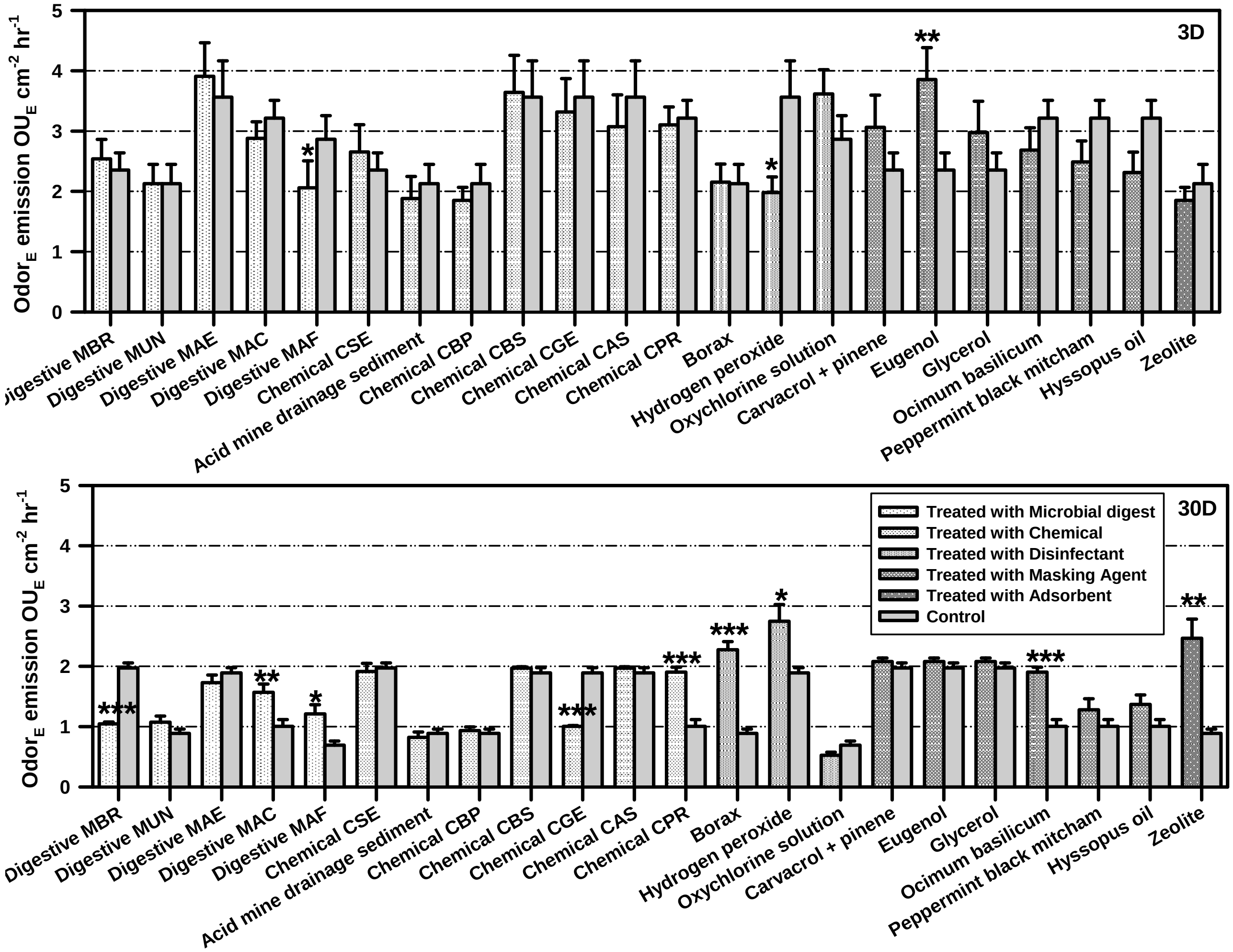

Figure 5. Mean odor emission rates and standard errors of dairy manure slurry with (treated) and without (Control) manure amendments stored at 20^oC for 3 d and 30 d. Each pair of amendment bars has Control on the right. Asterisks above treated bars indicate emission rates for one sample evaluated twice by 5 or 6 odor assessors (n=10 or 12) at each storage duration for significance from Control at P=0.05-0.01 (*); 0.01-001 (**); <0.0001 (***).

3.2 Odor Quality

None of the manure amendments tested had weak odor for both 3 and 30 d incubation. Using the ASTM OIRS supra-threshold intensity method, the average odor intensity of treated manure ranged from 628 to 3,245 ppm n-butanol in water for 3 d and from 636 to 2140 ppm n-butanol in water for 30 d incubation (Fig. 6). Overall, mean odor intensity was less for dairy manure incubated 30 d relative to manure stored for only 3 d. More offensive odorants were presumably degraded in the manure slurry over time.

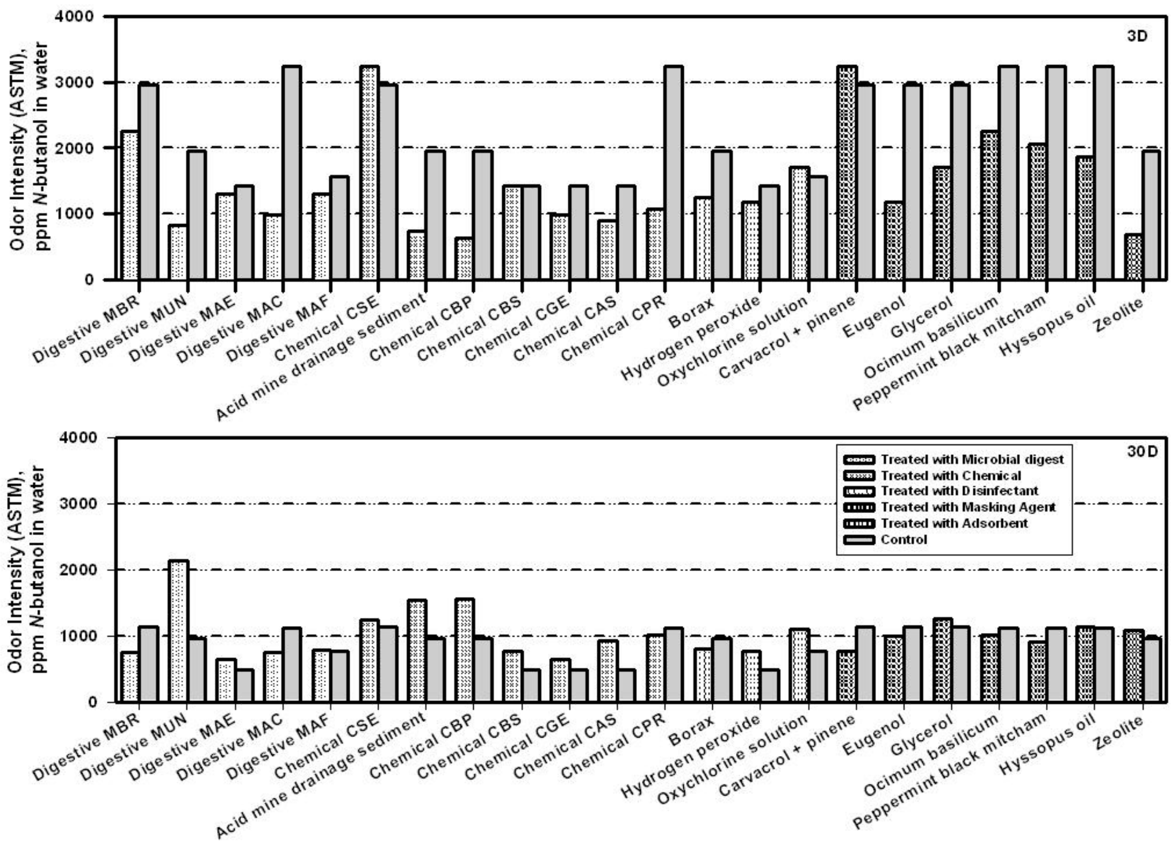

Figure 6. Mean odor intensity (ASTM, 2004) of dairy manure slurry with (treated) and without (Control) manure amendments stored at 20^{o}C for 3 d and 30 d. Each pair of bars shows Control manure on the right. (Note: Error bars are omitted due to subjective observation variability and transformation to arithmetic values from log 10 data used for determination of mean best estimate odor panel results.)

Most treatments (18 of 22) showed a reduction in mean supra-threshold odor intensity relative to Controls after 3 d storage although statistical significance could not be documented due to the highly variable nature of this measure. The lowest overall intensities at 3 d combined with dramatic reductions versus Control manure occurred in the zeolite treatment, digestives MUN and MAC, and chemicals CBP, CPR, and acid mine drainage treated manure. After 3 d storage the highest mean odor intensity was found in carvacrol +pinene essential oil and chemical CSE treated manure, both elevated over Control manure intensity. The essential oils are volatile compounds and can increase the manure odor emission. But with the exception of carvacrol + pinene, essential oils tended to reduce odor intensity with improved hedonic tone (as noted later).

At 30 d incubation only eight of the amendments offered improvement to supra-threshold odor intensity relative to Controls (Fig. 6). Odor intensity at 30 d was highest and most elevated over Control manure in digestive MUN treated manure while digestives MBR and MAC showed notably lower, improved intensity versus Control. This suggests that one diverse class of products, such as microbial additives, do not consistently improve odor performance. Across both storage periods, the greatest reductions in supra-threshold odor intensity were found in manure treated with digestive MAC and chemical CPR, followed by digestive MBR, borax, and eugenol. Following the Labeled Magnitude Scale method, mean odor supra-threshold intensity ranged between moderate (19) and very strong (44) for both storage periods.

Hedonic tone ranged from -2 to -6 indicating that none of the products had pleasant smell but this generally was an improvement versus Control manure. The most unpleasant hedonic tone was reported in untreated manure (-9.5) followed by manure treated with zeolite clinoptilotile (-9.0). The least unpleasant smell was reported for manure treated with essential oils (carvacrol +pinene, peppermint and *Hyssopus* oils) and chemicals oxychlorine and CPR. Generally, there was no consistent improvement in pleasantness when odor emitted after 3 d was compared to odor emitted from manure slurry aged 30 d, in contrast to observations of intensity and emission.

For all amendment products the treated and untreated manure gas had an earthy and offensive smell as reported by 27% to 67% of qualified odor assessors. Interestingly, manure treated with chemical amendments (i.e. AMD, CSE, CBP, CGE, CAS and CPR) had 33 to 60% of odor assessors report the odor as fruity in addition to being earthy and offensive. Manure treated with masking agents or essential oils had 27 to 54% of human panels reporting odor as fruity, floral, and medicinal, in addition to earthy and offensive. The microbial digestive amendments and untreated manure had the highest percentage of human panelists who reported the odor as offensive and earthy for both incubation periods. Odor descriptors used by assessors under the category of offensive included: manure, putrid, septic, sewer, urine, landfill leachate, and garbage.

Odor emissions were not correlated with odor intensity or hedonic tone of dairy manure (Fig. 7). Results suggest that the distinctive odor emitted from dairy manure, even when it is a less unpleasant smell with reduced strength, is still quickly detected as an odor emission by assessors. There was a relationship between hedonic tone and odor intensity (Fig. 8). Considering all treatments, the stronger the odor intensity, the more unpleasant the odor was described.

One salient finding in this screening trial was the significant and positive relationship of two methods for estimating odor intensity in dairy manure (Fig. 9). The correlation (0.830) values reported for odor intensity show that a subjective assessment of odor strength following the LMS method produced similar results with a quantitative description of odor strength using the ASTM method. This suggests that the ASTM method, which is relatively complex to implement, can be replaced with the simpler LMS method for evaluating odor strength in dairy manure

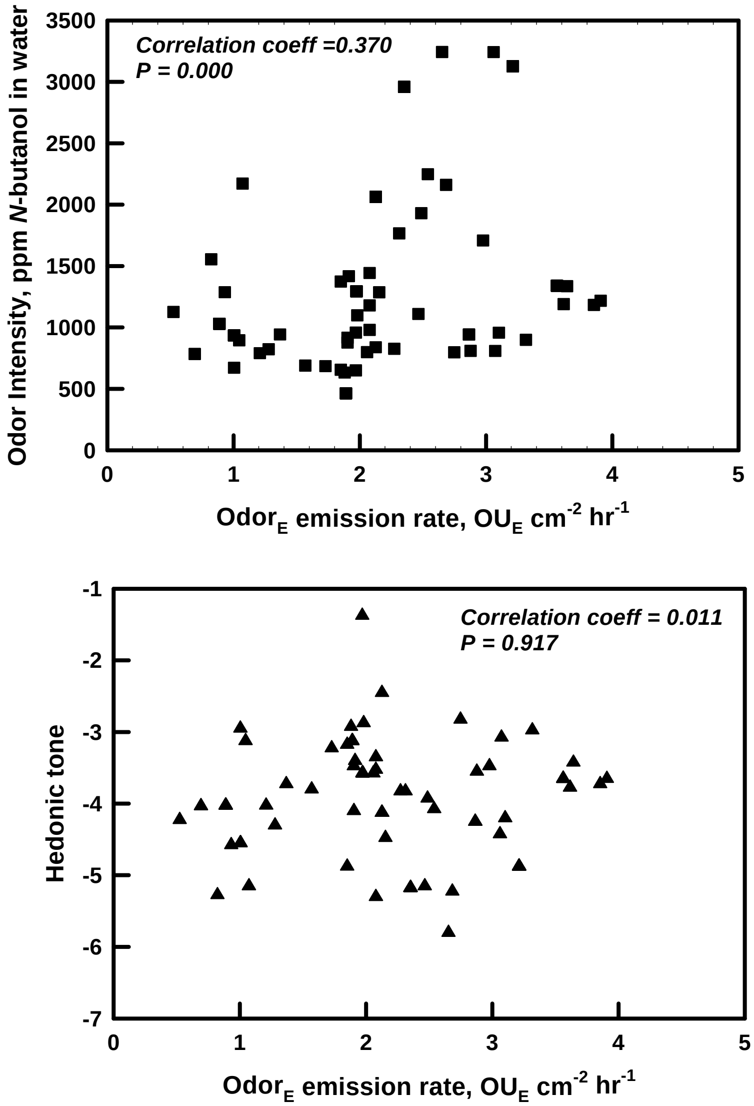

Figure 7. Lack of relationship of two subjective measures, odor intensity (top) and hedonic tone (bottom), with odor emission rate as determined by olfactometry.

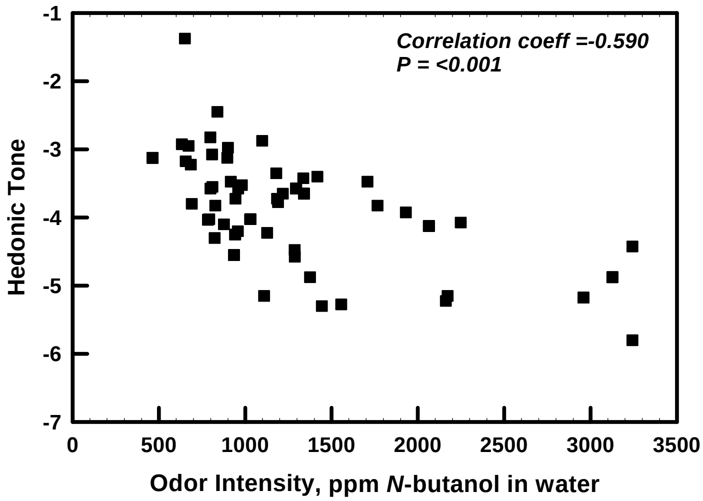

Figure 8. Relationship of hedonic tone and odor intensity using n-butanol in water (ASTM, 2004) method.

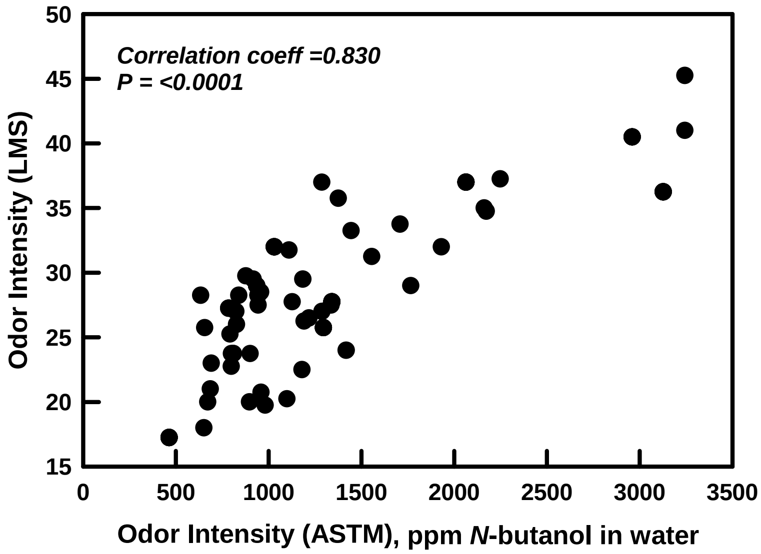

Figure 9. Relationship of odor intensity as evaluated with two methods: n-butanol in water (ASTM, 2004) and Labeled Magnitude Scale (LMS; Green et al., 1996).

4. CONCLUSIONS

None of the twenty-two amendments significantly reduced odor emission rates in dairy manure after both short and medium-term storage at warm (20^{o}C) conditions. Odor emission rates for virtually all compounds were significantly higher after 3 d than after 30 d. Storing dairy manure for 30 d under warm conditions reduced odor emission by 10 to 105% compared to emission at 3 d. Several amendments (some with repeated applications) significantly reduced odor depending on the storage period. The additions of a digestive aerobic/facultative microbe product MAF (Alken Enz Odor + Clear Flo), disinfectant hydrogen peroxide or essential oil *Hyssopus officinalis* to dairy manure offered short-term odor emission reduction. These products show promise for pre-land-application use if further study under field conditions can confirm the odor reduction potential. The essential oil amendment eugenol (clove) significantly increased odor emission after short term storage. Overall, none of the five classes of amendments consistently reduced odor emission in this study at 20^{o}C as measured via forced-choice olfactometry. Odor emission at 30 d storage was significantly reduced by almost half, compared to untreated manure, by two proprietary amendments with repeated application: digestive aerobic/facultative MBR (Bio-Regen) and chemical CGE (Greaseater). Overall, more treatments (7) significantly increased emission versus control manure after 30 d storage indicating that medium-term odor control remains challenging. All of the manure slurries treated with amendments had unpleasant smell, however they offered improvement over untreated manure evaluations. The essential oils typically offered short-term improvement to subjective measure of hedonic tone (pleasantness) and character descriptors. The majority of odor descriptors of treated manure cited by qualified assessors were offensive, earthy, medicinal, floral, and fruity. Hedonic tone was correlated with odor intensity while no relationship was found between odor emission rates and hedonic tone or odor intensity. A simplified odor intensity method, Labeled Magnitude Scale, was found to be essentially equivalent to the ASTM OIRS n-butanol-scaled method for evaluating supra-threshold odor strength.

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