

7-2005

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## **Abstract**

A laboratory air emission evaluation system consisting of eight emission vessels (19 L each) has been developed and used to investigate the effects of bio/chemical agents or feed additives on ammonia and odor emissions from poultry manure. A novel approach was used to evaluate volatile organic compounds (VOCs) and odor emissions, featuring air sampling with carboxen/PDMS 85 micrometer SPME fibers and analysis of the air sample with a state-of-the-art GC-MS-Olfactometry system, which allows for simultaneous chemical and olfactory analysis of air.

Clinoptilolite zeolite was surface-applied to 2.5 kg fresh laying hen manure at a rate of 0, 2.5%, 5% or 10% (0, 3.125, 6.25, 12.5 kg·m<sup>-2</sup> respectively). Cumulative ammonia emission over a two-week storage period was reduced by 20%, 50% and 77%, respectively, for the 2.5%, 5% and 10% regimens. Application of 2.55 kg·m<sup>-2</sup> (5% by weight) zeolite to a dynamically growing manure pile reduced ammonia emission by 44%. In another study, ammonia emission from stored manure of laying hens fed standard or modified diet was measured and compared. Cumulative ammonia emission from manure of the modified diet over the two-week storage time was 41% less than that from manure of the standard diet.

Thirty major VOCs including mercaptans, amines, amides, aldehydes, VFAs, phenolics and indolics identified with Mass Spectrometry Detector (MSD) were selected for comparison for zeolite single treatment. In addition, distinct odors/aromas with wide-ranging character descriptors and intensity determined by human nose were also compared. Consistent emission reduction was shown for trimethyl amine, VFAs, 4-ethyl-phenol and skatole, with relatively lower odor intensity. Dimethyl trisulfide was substantially increased in 10% treatment. The effects of zeolite on reduction or generation of VOCs were generally proportional to the application rate. Overall odor in poultry manure was controlled by zeolite treatment.

Ongoing studies will continue to identify, quantify and optimize other alternative agent(s) or diet manipulation to effectively reduce gaseous emissions from poultry manure.

## **Keywords**

Ammonia emission mitigation, air quality, manure storage, SPME, odor, GC-Olfactometry

## **Disciplines**

Bioresource and Agricultural Engineering

## **Comments**

This is an ASAE Meeting Presentation, Paper No. 054160.



*The Society for engineering  
in agricultural, food, and  
biological systems*

*An ASAE Meeting Presentation*

*Paper Number: 054160*

## **Evaluation of Treatment Agents and Diet Manipulation for Mitigating Ammonia and Odor Emissions from Laying Hen Manure**

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**Written for presentation at the  
2005 ASAE Annual International Meeting  
Sponsored by ASAE  
Tampa Convention Center  
Tampa, Florida  
17 - 20 July 2005**

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## Introduction

Ammonia (NH<sub>3</sub>) volatilization from intensive livestock operation not only reduces fertilizer nitrogen (N) value of manure, but also contributes to environmental pollution. Cost-effective technologies that reduce ammonia loss during animal housing, manure storage and land application will have positive economic and environmental benefits.

Layer manure is typically stock-piled either underneath cages in the lower level of high-rise houses or removed from belt layer houses to manure storage facilities once to seven times a week. Various mechanisms are involved in conserving N in poultry manure during storage, including immobilization of ammonium through addition of easily decomposable, N-poor materials, adsorption of ammonium (NH<sub>4</sub><sup>+</sup>) and NH<sub>3</sub> on suitable amendments, and pH regulation of the manure solution (Kirchmann and Witter, 1989).

Numerous additives have been investigated to reduce NH<sub>3</sub> volatilization from livestock manure. McCroy and Hobbs (2001) published a comprehensive review of a wide range of additives, i.e. acidifying agents, absorbing agents, and bacterial additives, for reducing ammonia and odor emission from livestock wastes.

Natural zeolite is a cation-exchange medium that has high affinity and selectivity for NH<sub>4</sub><sup>+</sup> ions due to its crystalline, hydrated properties resulted from the infinite, 3-dimensional structures (Mumpton and Fishman, 1977). It has been widely used as amendment to poultry litter (Maurice et al., 1998; Nakaue and Koelliker, 1981b), in anaerobic digesters treating cattle manure (Borja et al., 1996), during composting of pig slurry and poultry manure (Bernal et al., 1993; Kithome et al., 1999), air scrubber packing material to improve poultry house environment (Koelliker et al., 1980), and as a filtration agent in deep-bedded cattle housing (Milan et al., 1999). Kithome et al. (1998) investigated the kinetics of NH<sub>4</sub><sup>+</sup> adsorption and desorption by natural zeolite clinopilolite ((Na<sub>4</sub>K<sub>4</sub>)(Al<sub>8</sub>Si<sub>40</sub>)O<sub>96</sub>·24H<sub>2</sub>O) for its ability to adsorb N in its NH<sub>4</sub><sup>+</sup> form at various pH values and initial NH<sub>4</sub><sup>+</sup> concentrations.

Efforts were also made to investigate feed additives as a means to bind excreted N and other compounds so that ammonia and odor emission can be reduced at the source. Studies were conducted by feeding varying amount of zeolite to white leghorn layers (Nakaue and Koelliker, 1981a) or broiler chickens (Amon et al., 1997) to determine its effect on production parameters and fecal ammonia production. No consistent lowering trend of fecal ammonia evolution rate was observed between the fecal samples from layers fed 0 and 10% clinopilolite (Nakaue and Koelliker, 1981a). In a farm-scale study, Amon et al. (1997) used zeolite both as feed additive to broiler chickens (2% by weight) and litter treatment (total 1.6 kg·m<sup>-2</sup> at week 1, 4, 5 and 6). They reported 50% higher ammonia emission from treatment than from control. However, their results may be complicated by the higher temperature (2-3 °C) and higher litter moisture content (5-10%) observed in treatment room than control room. Miner and Stroh (1976) reported that

surface-applied zeolite consistently reduced  $\text{NH}_3$  release from cattle feedlot as compared to untreated surfaces. Nakaue and Koelliker (1981b) reported lower litter moisture and  $\text{NH}_3$ -N concentrations with zeolite clinopilolite at 2.5 or 5  $\text{kg} \cdot \text{m}^{-2}$  application rates on wood shavings after 21 days.

Limited success has been reported of using zeolite as odor control for livestock manure. Miner and Stroh (1976) found zeolites ineffective in reducing odor intensity from a cattle feedlot using Scentometer approach. No significant reduction of odor concentration and emission was found from broiler houses in which zeolite was used jointly as both feed additive and litter treatment (Amon et al., 1997). Among chemical additives, Varel (2001) reported that certain plant-derived essential oils are effective in controlling volatile fatty acids production in cattle waste, partly due to their antimicrobial action.

The objective of this study was to evaluate the efficacy of additives as either on-farm manure treatment or feed amendments for reducing ammonia and odor emission from laying hen manure. This paper reports the initial findings from an on-going study.

## **Materials and Methods**

### ***Emission Apparatus***

Eight emission vessels were constructed and housed in an environmentally controlled room in the LEAP Lab II of National Swine Research and Information Center at Iowa State University. The vessels were in cylinder shape with a volume of 19 L. The interior wall of each vessel was lined with Teflon FEP100 film (200A, DuPont Teflon © Films, Wilmington, DE). The vessels were covered with tight lids, which are also interiorly lined with Teflon film. Air inlet and outlet were located on the lid. Teflon tubing (1/4" diameter), manifold and nylon compression fittings were used in constructing the emission vessel system.

The vessels were operated under positive pressure. A diaphragm pump (Model DOA-P104-AA, Gast Manufacturing, Inc., Benton Harbor, MI) was used to supply fresh air to the emission vessels. The fresh air flow rate was adjusted by a mass flow controller (0 to 30 LPM, stainless steel wetted part, Aalborg Instruments and Control Inc., Orangeburg, N.Y.), which delivers air into a gas distribution manifold. Air was further divided by eight identical flowmeters (0.2 to 4 LPM, stainless steel valve, VFB-65-SSV, Dwyer Instruments, Inc., Michigan City, Indiana). A flow rate of 3 LPM was introduced into each vessel, leading to an air exchange rate of about 11 air changes per hour (ACH). Each vessel was equipped with a small fan hanging 6 cm under the lid for uniform gas mixing (12VDC, Radio Shack). Gas exhausted from the vessels was connected to a common 5 cm (2") PVC pipe, which was routed to the building vent outlet.

Exhaust air from each of the eight vessel headspace, incoming air and room air were sampled sequentially at 6-min intervals, with the first 4-min for stabilization and the last 2-min for measurement. This yielded a measurement cycle of one hour. A photoacoustic IR analyzer (Chillgard RT Refrigerant Monitor, MSA, Pittsburg, PA) was used to measure ammonia concentration. The analyzer uses an internal pump to draw air at a flow rate of approximately 1.0 LPM. Sequential sampling was controlled by eight solenoid valves (Type 6014, 24V, stainless steel valve body, Burkert Contromatic USA, Irvine, CA). Teflon filter was placed in front of each solenoid valve. Manure temperature was measured by type T thermocouples (0.2 °C resolution). Temperature and humidity of the room air were monitored with a temp/RH data logger (HOBO Pro RH/Temp, Onset Computer Corporation, Bourne, MA).

Analog outputs from thermocouples, NH<sub>3</sub> analyzer and mass flow controller were recorded at 20-s intervals using a measurement and control module (Model CR10, Campbell Scientific, Inc., Logan, Utah). Solenoid valve switching was controlled by a relay controller (SDM-CD 16AC, Campbell Scientific, Inc.).

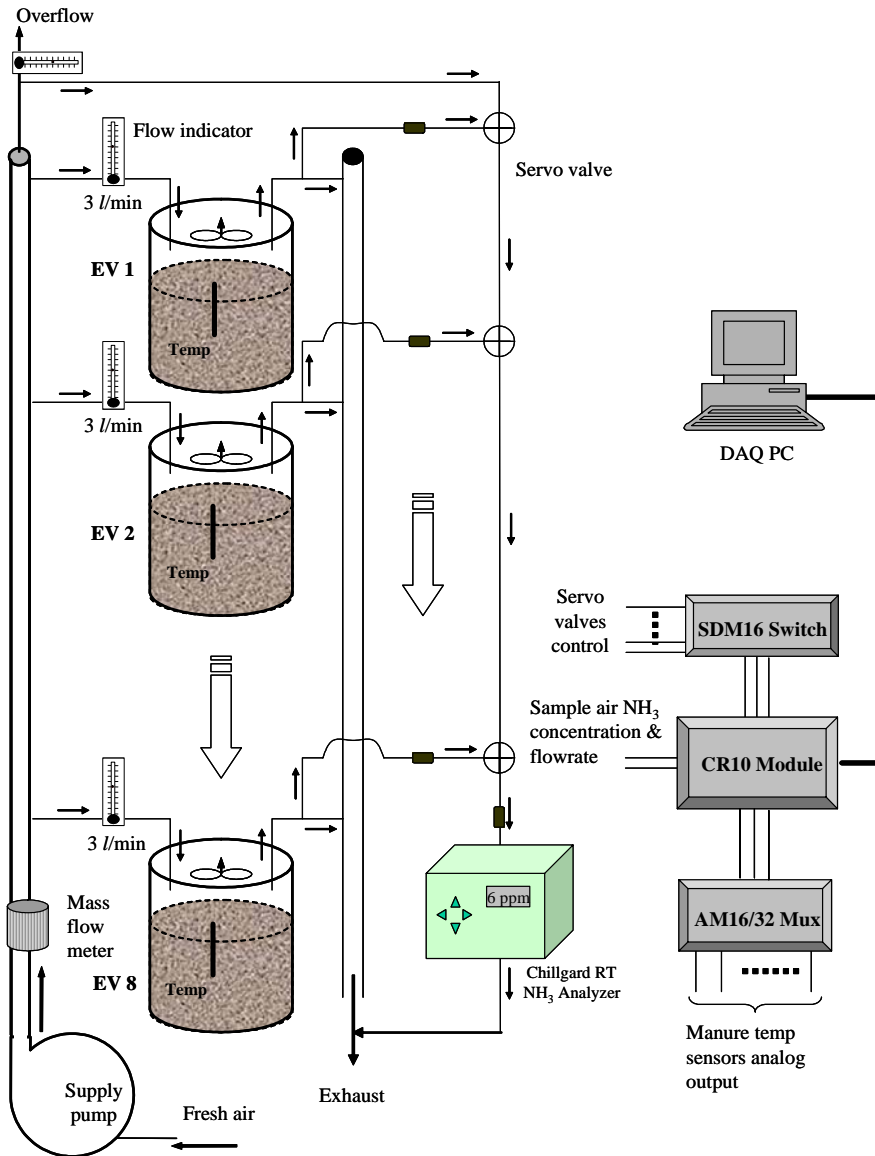


Figure 1. Schematic representation of the experimental setup for evaluating efficacy of treatment agents on ammonia emission reduction from laying hen manure (EV = emission vessel).

### **Sampling and Analysis of VOCs and Odor**

Solid phase microextraction (SPME) using 1-cm Carboxen-PDMS 85- $\mu$ m fiber (Supelco, Bellefonte, PA) was used for sampling headspace above the poultry manure in the vessels. SPME collections were carried out by direct fiber exposure in the dynamic headspace of vessels for 10 min. The extraction procedure was carried out at room temperature. Multidimensional

gas chromatography-mass spectrometry-olfactometry (MDGC-MS-O, Microanalytics, Round Rock, TX) was used for all analyses. The system utilizes conventional GC-MS (Agilent 6890N GC / 5973 MS, Agilent Inc., Wilmington, DE) as the base platform with the addition of an olfactory port and flame ionization detector (FID). The system was equipped with a non-polar precolumn and polar column in series as well as system automation and data acquisition software (MultiTrax™ V. 6.00 and AromaTrax™ V. 6.61, Microanalytics and Chemstation™, Agilent). The general run parameters used were as follows: injector, 260 °C; FID, 280 °C; column, 40 °C initial, 3 min hold, 7 °C / min, 220 °C final, 10 min hold; carrier gas, helium. Mass/charge (m/z) ratio range was set between 33 and 280 amu. Spectra were collected at 6 per sec and electron multiplied voltage was 1000 V. The detector was auto-tuned weekly.

Samplings followed by immediate chemical and odor analyses for zeolite single treatments (Trial 1) were carried out on day 1, 2, 3, 8 and 9. All eight vessels were sampled on day 2, while only one of each of control and 10% treatment vessels were sampled on other days. Compounds present in the headspace above the manure were identified with three sets of criteria: (1) match of the retention time on the MDGC capillary column with the retention time of pure compounds run as standards; (2) matching mass spectrums of unknown compounds with BenchTop/PBM mass spectrometry library search system and spectrums of pure compounds; and (3) matching odor characters. Qualitative assessment of VOC abundance was measured as area counts under peaks for separated VOCs. Only the mass fragments above the detection threshold ( $10^5$  area count) were considered as informative and were subsequently used. The relative effectiveness of zeolite treatment was evaluated by comparing area counts of selected chemical compounds between control and 10% treatment.

Human panelists were used to sniff separated compounds simultaneously with chemical analyses. Odor/aromas caused by separated compounds were evaluated for characters, and intensity was evaluated as percentage peak height. Odor was evaluated by comparing number of odor/aroma events, the intensity of specific odorants, and total odor intensity.

## ***Experimental Procedure***

### ***Manure Treatment***

Fresh hen manure was collected from a commercial belt layer facility before each trial of the manure additives. About 2.5 kg of fresh manure was loaded into a 3.8 L container with 0.02 m<sup>2</sup> manure surface. Different amounts of zeolite (grade 14x40, Bear River Zeolite Company, Thompson Falls, MT) of 62.5 g, 125 g or 250 g were surface-applied on top of the manure, corresponding to an application rate of 3.125, 6.25, or 12.5 kg·m<sup>-2</sup> manure surface. Each container was placed in the 19 L vessel. Two vessels were used as controls with no zeolite application. Two trials (Trials 1 and 2) were conducted to achieve four replicates of each treatment. Each trial lasted for 14 days.

In Trial 3, equal amount of fresh manure (5 cm thickness, 2.5 kg per layer) was added to all vessels every other day for four layers to simulate manure removal from the belt hen houses into manure storage. Zeolite of 125 g (5% by weight) was surface-applied on top of each layer in four vessels while the other four served as control. Fresh manure was loaded directly into the 19 L vessel with 0.05 m<sup>2</sup> manure surface (as opposed to the smaller 3.8 L container, then placed inside the vessel). Zeolite application rate was 2.55 kg·m<sup>-2</sup> manure surface. The air exchange rates ranged from 11 to 21 air changes per hour (ACH) in each vessel, due to the increased manure volume from manure addition. Ammonia emission was continuously monitored for eight more days after the last manure addition (total of 14 days).

### ***Feed Additive***

In Trial 4, the effect of feed additives on ammonia emission from layer manure was tested. Fresh manure was collected from laying hens fed with either treatment ration (Ecocal) or standard industrial ration and kept frozen for one month before comparative test was conducted using the emission vessels. The treatment ration was custom-formulated by a cooperative producer, which consisted of gypsum (calcium sulfate, to partially replace limestone) and zeolite. Again 2.5 kg manure was loaded in each 3.8 L container and kept inside the 19 L ventilated emission vessel for 14 days. The treatment and control each had four replicates.

### **Manure Nutrient Analyses**

Samples of fresh and post-storage manure were collected and sent for chemical analyses in an EPA certified lab. Moisture content, total N content, ammoniacal N and pH were analyzed.

### **Statistical Analyses**

Daily and cumulative NH<sub>3</sub> ER data were analyzed for treatment effect using PROC GLM with mean comparison option in SAS.

## **Results and Discussion**

### **Manure Property**

Properties of fresh and post-storage manure are presented in Tables 1 and 2. Ammoniacal N contents of manure at the end of the trial were generally higher than those at the beginning. Kirchmann and Witter (1989) reported that in anaerobic manure about two-thirds of nitrogen was present as ammonium and about one-third as organic N. Presumably anaerobic condition dominated under the top surface due to the high moisture content. Anaerobic conditions induced acid formation and an accumulation of ammonium N.

Table 1. Characteristics of the layer manure at the beginning and end of trials 1 and 2.

Property	Beginning			End			
	Trial 1	Trial 2	Avg	Control	Trt2.5	Trt5	Trt10
Dry Matter (%)	26.6	23.9	25.3 (1.9)	29.1 (2.0)	26.3 (0.8)	23.4 (0.5)	24.6 (1.8)
Total N (%)	1.69	1.33	1.5 (0.3)	1.51 (0.2)	1.55 (0.1)	1.51 (0.1)	1.38 (0.2)
Ammoniacal N (%)	0.47	0.76	0.62 (0.2)	0.94 (0.1)	1.07 (0.1)	0.96 (0.03)	0.92 (0.07)
pH	7.1	7.8	7.5 (0.5)	7.7 (0.3)	7.8 (0.3)	7.7 (0.2)	7.6 (0.1)

Table 2. Characteristics of the layer manure at the beginning and end of trial 3.

Property	Beginning		End	
	Control	Treatment	Control	Treatment
Dry Matter (%)	26.4	31.0	31.4 (2.7)	31.8 (0.7)
Total N (%)	1.56	1.89	1.62 (0.08)	1.73 (0.2)
Ammoniacal N (%)	0.16	0.21	1.18 (0.11)	1.24 (0.08)
pH	6.5	6.2	7.9 (0.3)	7.7 (0.3)

### **Ammonia Emission**

#### Zeolite as Treatment Agent

Surface-applied zeolite on fresh manure substantially decreased NH<sub>3</sub> emission during 14-d storage period and the magnitude of emission reduction was generally proportional to the application rate (fig. 2). The adsorption of NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> took effect right after its application on day 0 and resulted in the highest ER reduction on day 1. Ammonia emissions were reduced by 66,



91 and 96% at the end of day 1, respectively, for application rate of 2.5, 5 and 10%. Daily  $\text{NH}_3$  ER of the control vessels became stabilized after day 3, while ERs of the treatment vessels continued to increase with the slope of Trt2.5 being the steepest. Ammonia ERs of Trt5 and Trt10 on every single day were significantly different from those of control ( $P < 0.01$ ). Ammonia ERs of Trt2.5 from day 1 to day 7 were significantly different from those of control ( $P < 0.01$ ).

Table 3 summarizes the daily average  $\text{NH}_3$  ER and cumulative  $\text{NH}_3$  ER for the zeolite trials (Trials 1, 2, 3). Cumulative  $\text{NH}_3$  ER reductions at the end of day 7 and day 14 were 68% and 20% for Trt2.5, 81% and 50% for Trt5, and 96% and 77% for Trt10. The 14-day average daily  $\text{NH}_3$  ERs were 0.231, 0.185, 0.116 and 0.053  $\text{g} \cdot \text{initial kg}^{-1} \text{d}^{-1}$  for control, Trt2.5, Trt5 and Trt10, respectively. Expressed on the basis of unit emitting surface area, the 14-day average daily  $\text{NH}_3$  ER was 29.9, 24.0, 15.0, 6.9  $\text{g} \cdot \text{d}^{-1} \text{m}^{-2}$  for the control, Trt2.5, Trt5 and Trt10, respectively. Nitrogen loss as  $\text{NH}_3$  was 18% for control vessels and 14.6%, 9.1%, and 4.2% for Trt2.5, Trt5 and Trt10 vessels, respectively (table 4). There was no significant difference in manure temperature among the vessels, averaging 23.5°C.

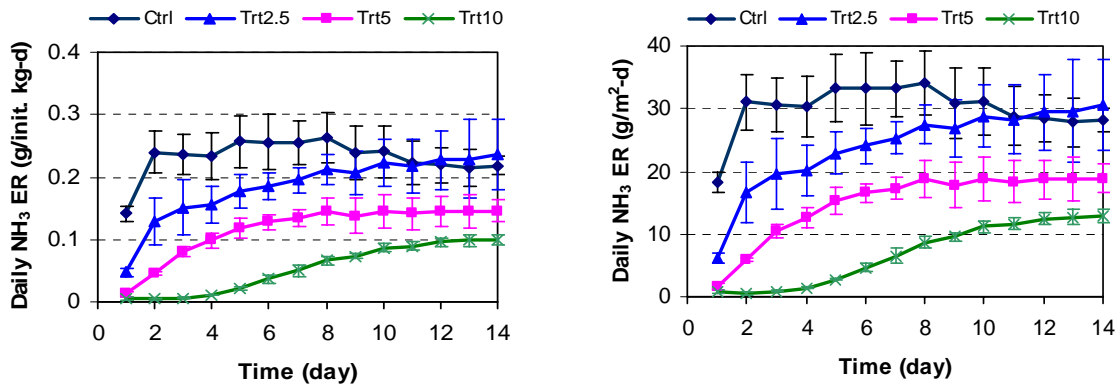


Figure 2. Daily ammonia emission rates of ventilated storage of fresh manure with various zeolite surface-application rates on day 0. Ctrl – no zeolite; Trt2.5 – zeolite 2.5% by weight; Trt5 – zeolite 5% by weight; Trt10 – zeolite 10% by weight.

Daily  $\text{NH}_3$  ER as well as daily manure and air temperatures for Trial 3 are shown in figure 3. Ammonia ER of the 2<sup>nd</sup> day after each manure addition (day 2, 4, 6, 8) was always higher than that of the 1<sup>st</sup> day (day 1, 3, 5, 7). Ammonia ER from treatment was reduced by  $70 \pm 2.5\%$  at the end of day 1 and  $48 \pm 1.2\%$  at the end of day 2. Cumulative  $\text{NH}_3$  ER by the end of day 8 was 54% lower from treatment manure than control. Nitrogen loss was 6.0% and 3.7% for control and treatment manure, respectively (table 4). There was no significant difference in manure temperature among the vessels, averaging 22.4°C.

Addition of second or more layer of manure in all vessels didn't seem to result in increased ammonia emission on a per vessel basis ( $\text{g} \cdot \text{d}^{-1}$  or  $\text{g} \cdot \text{m}^{-2} \text{d}^{-1}$ ), largely due to unchanged emitting surface in vessels. However, on a per unit mass of raw manure basis, daily ammonia ER decreased progressively with time (fig. 3). The result confirmed that the exposed surface layer mainly contributed to ammonia emissions from stacked poultry (hen) manure (Li et al., 2005).

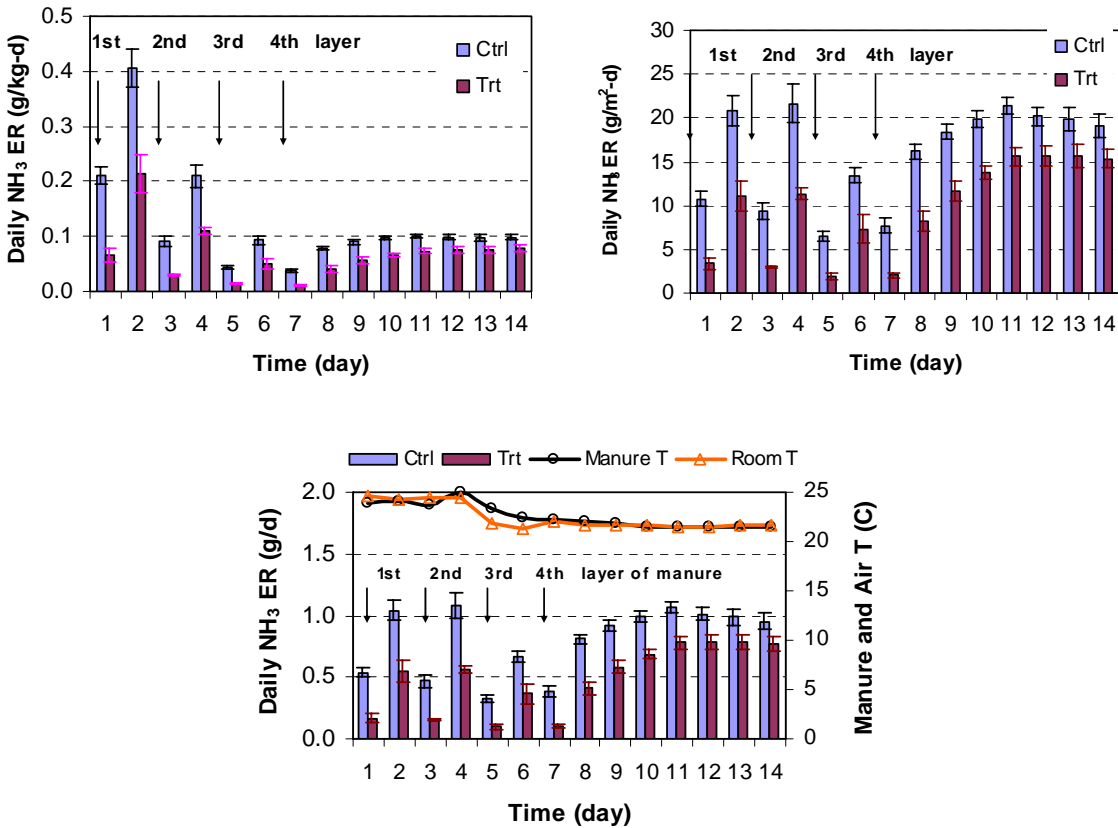


Figure 3. Daily ammonia emission rates of ventilated storage. Fresh manure was added at day 0, 2, 4, 6, with zeolite surface-application at day 0, 2, 4, 6. Ctrl – no zeolite; Trt – zeolite 5% by weight.

Table 3. Ammonia emissions from zeolite-treated poultry manure (Ctrl – no zeolite, Trt2.5 – 2.5% zeolite, Trt5 – 5% zeolite, Trt10 – 10% zeolite).

	Single Application				Four Layers	
	Ctrl	Trt2.5	Trt5	Trt10	Ctrl	Trt5
Application rate, kg·m <sup>-2</sup>	0	3.125	6.25	12.5	0	2.55
Avg. daily ER, g·d <sup>-1</sup>	0.60	0.48	0.30	0.14	0.80	0.49
Avg. daily ER, g·kg <sup>-1</sup> ·d <sup>-1</sup>	0.231	0.185	0.116	0.053	0.137	0.069
Unit area daily ER, g·m <sup>-2</sup> ·d <sup>-1</sup>	29.9	24.0	15.0	6.9	16.1	9.7
7-d cumulative ER, g·kg <sup>-1</sup>	1.6	1.0	0.62	0.14	-	-
7-d cumulative ER reduction	-	68%	81%	96%	-	33%*
14-d cumulative ER, g·kg <sup>-1</sup>	3.0	2.5	1.4	0.7	1.7	1.0
14-d cumulative ER reduction	-	20%	50%	77%	-	44%
8-d cumulative ER reduction	-	-	-	-	-	54%

\* represents cumulative ER reduction within 7 days after the last layer of manure

Kithome et al. (1999) reported that NH<sub>3</sub> loss was decreased by 44% when composting poultry manure over 56 days with a surface application of 38% zeolite. Bernal et al. (1993) also reported that more than 90% of N-loss was trapped by placing 12% (by weight) zeolite in air stream over 13-day composting of pig slurry and chopped straw mixture. Zeolite additions at 2.5% and 6.25% into dairy slurry reduced NH<sub>3</sub> emissions by 22% and 47%, respectively, over 4-d storage period (Lefcourt and Meisinger, 2001).

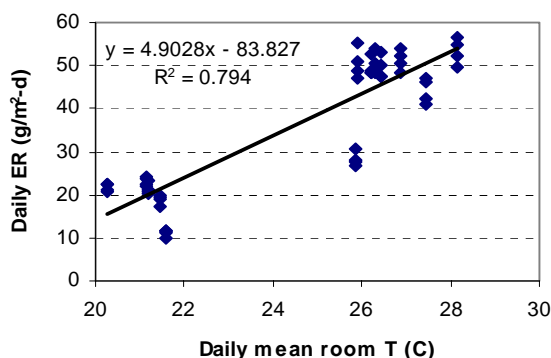


Figure 4. Correlation of daily ammonia emission and daily mean room temperature. Data collected from four control vessels.

During the trial period, temperature in the controlled room fluctuated between 21 to 28 °C, affected by a parallel study conducted in the adjacent room. Due to relatively small mass of manure used in each vessel (2.5 kg), the manure temperature closely followed room temperature. Trial 3 (feed additive) experienced the largest temperature fluctuation (21 to 28 °C). Daily NH<sub>3</sub> ER (g·m<sup>-2</sup>·d<sup>-1</sup>) collected from four control vessels revealed a positive linear relationship with daily mean room temperature (figure 4). A regression equation between the daily NH<sub>3</sub> ER and daily mean room temperature was of the following form:

$$ER = 4.9T_{room} - 83.8; \quad R^2=0.794$$

where ER is the unit area daily NH<sub>3</sub> emission rate (g·m<sup>-2</sup>·d<sup>-1</sup>), and T<sub>room</sub> is the daily mean room temperature (°C). Effect of storage temperature on manure ammonia emission warrants further investigation.

Table 4. Nitrogen loss (%) as ammonia during 14-day ventilated storage of fresh manure with or without zeolite treatment (mean ± S.D.)

	Ctrl	Trt2.5	Trt5	Trt10	Trt
A single application of different rates	18.0 (2.1)	14.6 (0.8)	9.1 (0.6)	4.2 (0.4)	
Four layers of manure + Zeolite surface application	6.0 (0.2)				3.7 (0.2)
Manure with feed additive	21.6 (0.5)				10.4 (0.8)

#### Feed Additive

Figure 5 shows the daily NH<sub>3</sub> ER as well as daily manure and air temperatures for both feed amended manure and control manure. Mean daily ammonia emission over 14 days were 0.29 g·kg<sup>-1</sup> d<sup>-1</sup> for control and 0.17 g·kg<sup>-1</sup> d<sup>-1</sup> for treatment (table 4), an average reduction of 41%. Daily NH<sub>3</sub> ER of the treatment after day 2 was significantly lower than the corresponding ER of the control (P<0.01). Emission reduction in the treatment manure was achieved by a combination of acidogenic material (gypsum) and NH<sub>4</sub><sup>+</sup> absorbing material (zeolite). Protonation was induced by a lower pH caused by gypsum and NH<sub>4</sub><sup>+</sup> ion was removed from NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> equilibrium by zeolite.

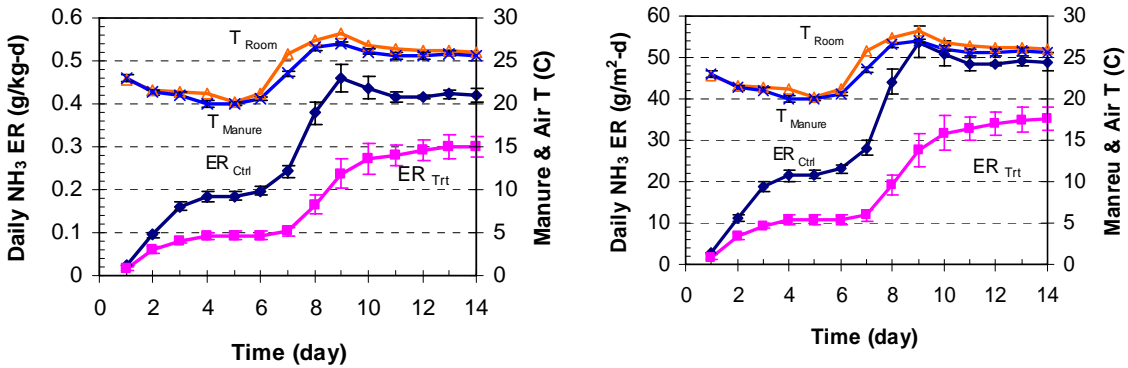


Figure 5. Daily ammonia emission rates and manure or air temperatures of stored poultry manure from laying hens fed either standard ration or the treatment ration.

### VOCs and Odor Evaluations

Thirty compounds (out of 91 that were identified) were selected for comparisons of treatment effects. These compounds represented a mix of major malodorous compounds and/or compounds that were present in large amounts in the headspace. Selected compounds included mercaptans, amines, amides, aldehydes, volatile fatty acids, phenolic and indolic compounds. Area counts of 30 chemical compounds from all eight vessels on day 2 were shown in figure 6. Certain compounds i.e. trimethyl amine, petanoic acid, etc., were not detected in any treatment manure due to amount being lower than detection threshold. Heptanal, 2-mythel propanamide, propanamide and butanamide were included in figure 6 since they were detected later on days 8 and 9.

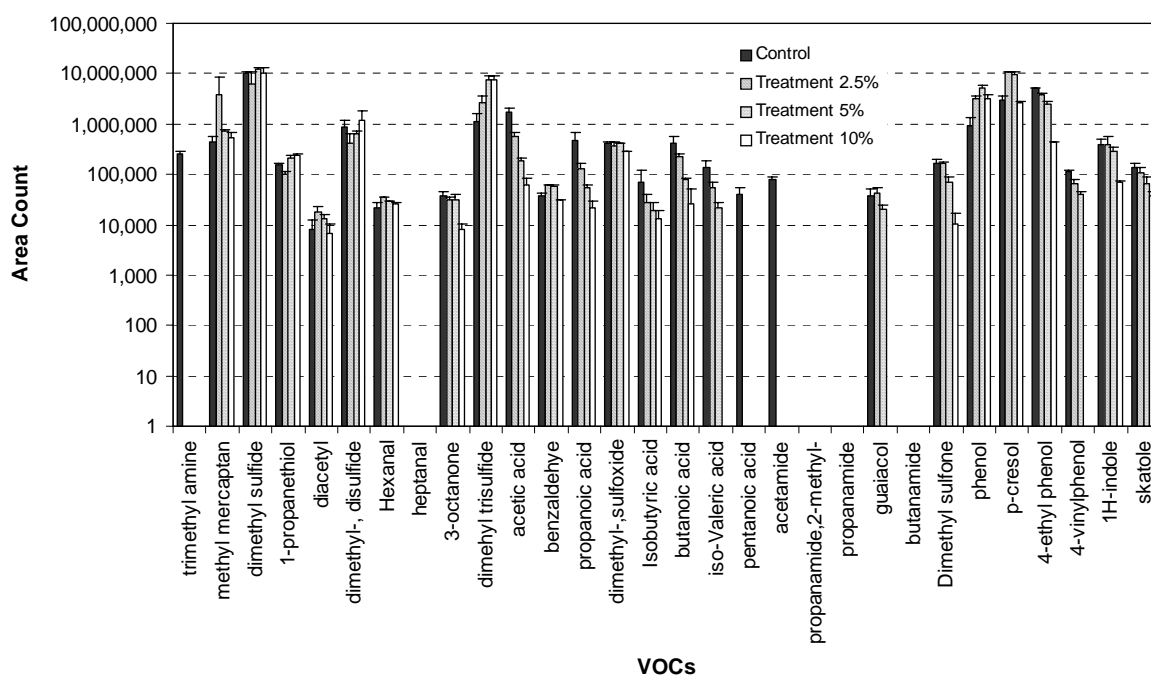


Figure 6. Area counts of selected chemical compounds from four treatments on day 2. Error bars represent standard deviation (n=2).

The 30 chemical compounds were evaluated for relative effectiveness by calculating percentage reduction of 10% treatment against control. A compound with a hundred percent value represented no detection of it from 10% treatment, while compounds with negative percentage represent increased area count found in 10% treatment than control. Most VFAs (volatile fatty acids) as well as certain major odorants (4-ethyl phenol, skatole) were reduced in 10% treatment. Dimethyl trisulfide was substantially increased in 10% treatment. The decay and generation of specific VOCs appears to be a function of storage time.

Table 5. Relative reduction of selected chemical compounds by 10% zeolite treatment in stored poultry manure (units as %)

Compound Name	Ion (m/z)	Day 1	Day 2	Day 3	Day 8	Day 9	Mean	Standard Deviation
<b>Positive Treatment Effect</b>								
trimethyl amine	58	100	100	100		100	100	0
2,3-butanedione(diacetyl)	86	100	22	24	55	4	41	38
heptanal	70				72	24	48	34
3-octanone	99	84	77	76	100		84	11
acetic acid	60	34	97	100	100	94	85	28
benzaldehyde	106	70	12	2	84	66	47	37
propanoic acid	74	44	95	96	100	100	87	24
iso-Valeric acid	60		100	100	100	99	100	0
pentanoic acid	60		100		100	92	97	5
acetamide	44		100		100	66	89	20
propanamide,2-methyl-	59				100	100	100	0
propanamide	57				100	86	93	10
phenol,2-methoxy-	124	89	81	78			83	6

(guaiacol)								
butanamide	72			100	97	98	2	
Dimethyl sulfone	79	85	96	100	100	92	95	6
4-ethyl phenol	107	68	91	80	32	10	56	34
1H-indole	117	94	76	73	43	56	68	20
skatole	130	84	70	100	51	71	75	18
<b>No Apparent Effect</b>								
butanoic acid	60	-12	97	95	99	96	75	49
dimethyl-,sulfoxide	63	-75	27	57	85	14	21	61
Isobutyric acid	73	-79	45	100	100	100	53	78
4-vinyl phenol	120	100	100	83	43	-18	62	50
Hexanal	56	57	-41	-25	100	100	38	68
p-cresol	107	97	-8	-20	2	-11	12	48
dimethyl sulfide	62	-146	5	-43	19	-334	-100	146
dimethyl-, disulfide	79	-327	-45	20	77	45	-46	163
phenol	94	91	-498	-247	71	62	-104	261
methyl mercaptan	47	-113	-32	-65	31	-22	-40	53
1-propanethiol	76	-256	-70	-66	2	-221	-122	111
<b>Negative Treatment Effect</b>								
dimehyl trisulfide	126	-1908	-1002	-4201	-1294	-1268	-1935	1310

The effects of the 10% zeolite treatment on total odor emitted from poultry manure are presented in table 6 and figure 7. Total odor, quantified as the total peak area for all odor and aroma events, in the control sample always appeared to be higher than in the 10% zeolite treatment. Thus, the overall odor in poultry manure was reduced by zeolite treatment.

Table 6. Relative reduction of major odorant compounds by 10% zeolite treatment in stored poultry manure (units as %)

Odor (Compound)	Day 1	Day 2	Day 3	Day 8	Day 9
Buttery (diacetyl)	66	31	8	69	
Grassy (hexanal)	0	84	77	100	8
Onion/burn food/fatty acid (benzaldehyde)	92		55	100	100
Body odor (isovaleric acid)	100	96	96	100	100
Burnt (Guaiacol)	100	84	99	100	100
Phenolic (Phenol)	100	86	91	100	100
Phenolic/Barnyard (p-cresol)	100	100	70	100	100
Burnt/Phenolic/Medicinal (4-ethyl phenol)	100	97	84	100	44
Barnyard (Skatole)	21	98	80	54	
Fecal (Trimethyl amine)	100	100	100	-10	14
Sewer (H2S)	-11	15	28		0
Onion (1-propanethiol)		-61	20		22
Barnyard (1H-Indole)	100	55	-118	55	
Burnt (dimethyl-, disulfide)	-223	0	24		60
Fatty acid/ Body odor (butanoic acid)	100	97	-2,587	100	100

Fecal (Methyl mecaptan)	30	-46	63	-46	14
Onion (Dimethyl sulfide)	-240	-12	-5	64	
Onion (Dimethyl trisulfide)	65	-98	-123	-59	-672

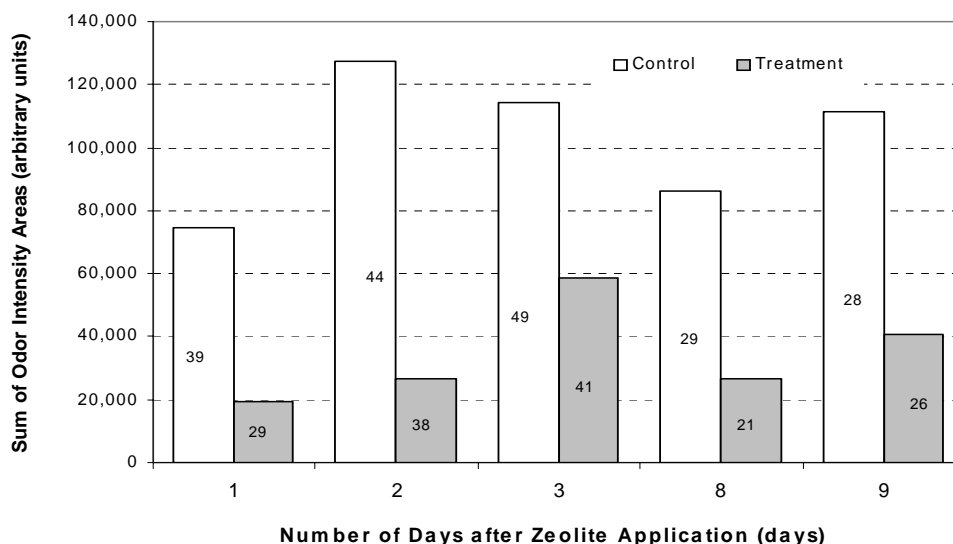


Figure 7. Overall odor intensity from headspace of control and 10% zeolite treatment. Numbers in bars represent total odor and aroma events.

### ***Economic Implication***

Zeolite used in this study (grade 14x40) cost about \$0.12 per lb (truck load). Assuming a daily manure excretion of 120 g·hen<sup>-1</sup> d<sup>-1</sup>, the daily manure loading rate from a 100,000 laying hen facility into a storage facility would be 12,000 kg·d<sup>-1</sup> (ignore drying on belt), which approximates 12 m<sup>3</sup>·d<sup>-1</sup>. This amount will cover a surface area of 240 m<sup>2</sup> assuming a 2-inch (5 cm) thickness of new manure layer on existing pile. An application of 2.55 kg·m<sup>-2</sup> zeolite would represent a treatment cost of \$161 per 100,000 birds per day or an annual treatment cost of \$0.59 per hen. Cost could presumably be lowered if the thickness of manure layers is doubled.

The estimated additional wholesale cost of Ecocal amended feed was \$7.00/ton of feed. Assuming a feed consumption of 0.22 lb·day<sup>-1</sup> hen<sup>-1</sup>, Ecocal amendment represents an annual added cost of \$0.28 per hen.

### **Conclusions**

Surface-application of zeolite onto laying hen manure is effective in reducing NH<sub>3</sub> emission during storage. A single application of 3.125, 6.25, 12.5 kg zeolite·m<sup>-2</sup> manure surface reduced NH<sub>3</sub> losses by 20, 50, 77% during a 14-day ventilated storage. Top dressing of zeolite at 2.55 kg·m<sup>-2</sup> onto manure accumulation in a simulated manure loading into storage (every two days for eight days, i.e., four layers) reduced NH<sub>3</sub> emission by 58%. Daily NH<sub>3</sub> emissions from feed amended manure were significantly lower than those from control manure. Cumulative ammonia emission during 14-day ventilated storage was 41% lower from feed amended manure than that of control manure. Most VFAs (volatile fatty acids) as well as certain major odorants (4-ethyl

phenol, skatole) were reduced in 10% zeolite treatment. The overall odor in poultry manure was controlled by zeolite treatment.

## Future Studies

Work is on-going to test and compare other manure agents and feed additives for mitigating NH<sub>3</sub> emission. Soapstock, a soybean processing byproduct, and alum will be compared for their effectiveness in controlling NH<sub>3</sub> and odor emission from layer manure storage as well as economics.

## Acknowledgements

Funding for the study was provided in part by the U.S. Poultry and Egg Association and is acknowledged.

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