

1-2007

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Lingshuang Cai
Iowa State University

Jacek A. Koziel
Iowa State University, koziel@iastate.edu

Yi Liang
Iowa State University

Anh Thu Nguyen
Iowa State University

Hongwei Xin
Iowa State University, hxin@iastate.edu

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Abstract

Poultry operations are associated with emissions of aerial ammonia (NH₃), volatile organic compounds (VOCs), and odor, and the magnitude of emissions is influenced by manure management practices. As a manure treatment additive, zeolites have been shown to have the potential to control NH₃. Because of their properties it is also expected that zeolites could effectively adsorb VOCs and odor. The effectiveness of zeolite in controlling odor and VOCs was qualitatively evaluated in this controlled laboratory study involving simulated poultry manure storage. In the first two trials, zeolite was topically applied on nearly fresh laying hen manure at the rates of 0, 2.5, 5, and 10% (by weight). In the third trial, zeolite was topically applied at 5% with each addition of fresh manure into the storage vessel. Headspace samples from the emission vessels were collected with solid phase microextraction (SPME) and analyzed on a multidimensional-gas chromatograph-mass spectrometry-olfactometry (MDGC-MS-O) system for identification and prioritization of poultry manure odorants. Acetic acid, butanoic acid, isovaleric acid, indole, and skatole were consistently controlled in the headspace, with the reduction rate being proportional to the zeolite application rate. Dimethyl trisulfide and phenol were consistently generated, and with a few exceptions, the rate of generation was proportional to the application rate. Average reduction of the odor caused by all odorants evaluated with SPME-GC-O was 67% ($\pm 12\%$) and 51% ($\pm 26\%$) for the two topical applications, respectively, while no significant reduction of VOCs and odor was detected for the layered application.

Disciplines

Bioresource and Agricultural Engineering | Environmental Health | Poultry or Avian Science

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This is a manuscript of an article published as Cai, Lingshuang, Jacek A. Koziel, Yi Liang, Anh Thu Nguyen, and Hongwei Xin. "Evaluation of zeolite for control of odorants emissions from simulated poultry manure storage." *Journal of Environmental Quality* 36, no. 1 (2007): 184-193. DOI: [10.2134/jeq2006.0052](https://doi.org/10.2134/jeq2006.0052). Posted with permission.

**Evaluation of zeolite for control of odorants emissions from simulated poultry
manure storage**

**Lingshuang Cai^{a,b}, Jacek A. Koziel^{a*}, Yi Liang^{a,c}, Anh Thu Nguyen^a,
Hongwei Xin^a**

**^aDepartment of Agricultural and Biosystems Engineering, Iowa State University, Ames,
Iowa, 50011, USA;**

***corresponding author: koziel@iastate.edu, phone: 515-294-4206**

^bDepartment of Chemistry, Wuhan University, Wuhan 430072, PR China.

^cCurrent address: USDA-ARS, Pendleton, Oregon, USA.

ABSTRACT

Poultry operations are associated with emissions of aerial ammonia (NH_3), volatile organic compounds (VOCs), and odor, and the magnitude of emissions is influenced by manure management practices. As a manure treatment additive, zeolites have been shown to have the potential to control NH_3 . Because of their properties it is also expected that zeolites could effectively adsorb VOCs and odor. The effectiveness of zeolite in controlling odor and VOCs was qualitatively evaluated in this controlled laboratory study involving simulated poultry manure storage. In the first two trials, zeolite was topically applied on nearly fresh laying hen manure at the rates of 0, 2.5%, 5% and 10% (by weight). In the third trial, zeolite was topically applied at 5% with each addition of fresh manure into the storage vessel. Headspace samples from the emission vessels were collected with solid phase microextraction (SPME) and analyzed on a multidimensional-gas chromatograph-mass spectrometry-olfactometry (MDGC-MS-O) system for identification and prioritization of poultry manure odorants. Acetic acid, butanoic acid, isovaleric acid, indole and skatole were consistently controlled in the headspace, with the reduction rate being proportional to the zeolite application rate. Dimethyl trisulfide and phenol were consistently generated, and with a few exceptions, the rate of generation was proportional to the application rate. Average reduction of the odor caused by all odorants evaluated with SPME-GC-O was 67% ($\pm 12\%$) and 51% ($\pm 26\%$) for the two topical applications, respectively, while no significant reduction of VOCs and odor was detected for the layered application.

INTRODUCTION

Emissions of aerial pollutants from high-density poultry and livestock facilities are of increasing public concern (National Research Council, 2003). The anaerobic nature of manure stabilization can cause offensive odors and release of ammonia (NH_3), hydrogen sulfide (H_2S) along with various volatile organic compounds (VOCs) during the collection, transfer, storage, treatment and subsequent land application (Bicudo et al., 2002). Ammonia is the abundant gas emitted from poultry manure, but VOCs and odor are also of concern. The environmental problems associated with poultry manure could be mitigated through application of treatment additives. Numerous types of additives have been used to reduce NH_3 and odor emissions from livestock wastes (McCrary and Hobbs, 2001). Zeolites are one of such additives and have a high surface area and cationic exchange properties (Mumpton and Fishman, 1977). Natural zeolite (clinoptilolite) has been shown to have the potential to control ammonium ion in wastewater (Komarowski and Yu, 1997). These properties and the abundance of low-cost zeolite-bearing deposits have made it an attractive option for a variety of applications in the treatment of livestock and poultry wastes. Clinoptilolite has been investigated as both a livestock feed additive and a topical manure additive to adsorb NH_3 . Application directly to the manure seems to be more effective in reducing NH_3 emissions (Liang, et al., 2005; Miner, et al., 1997; Witter and Kirchmann, 1989), although addition through the feed is a more practical application (McCrary and Hobbs, 2001).

The same physicochemical properties that make zeolite so attractive for NH_3 abatement are also expected to enhance adsorption of VOCs and odor emitted from poultry and livestock

wastes. The mechanism of VOCs and odor control from livestock slurries has been attributed to the high adsorptive capacities of zeolites (Pain et al., 1987). Japanese farmers have sprinkled zeolite on farmyard and manure piles for years to control both odor and moisture content (Mumpton, 2006). Miner and Stroh (1976) evaluated several materials including clinoptilolite and erionite as surface applications to cattle feedlots for NH_3 and odor control. These two zeolites were then judged to be somewhat effective for odor control (Miner and Stroh, 1976). The use of erionite is currently phased out due to inhalation health hazards. No significant reduction of odor concentration and odor emissions were found from broiler houses where zeolite was used simultaneously as feed additive and topical litter treatment (applied only in week 1, 4, 5 and 6 of the study) in a broiler operation in Slovenia (Amon et al., 1997). A reduction of odor intensity was observed when a simple air scrubber packed with clinoptilolite was used inside a laying hen house (Koelliker et al., 1980).

The majority of the literature related to VOCs emitted from livestock manure stem from studies of swine manure (Schaeffer, 1977; O'Neal and Phillips, 1992; Schiffman, et al., 2001). To date, relatively little is known about the chemical nature of odorous compounds in poultry manure beyond the early studies when gas chromatography became available (Deibel, 1967; Burnett, 1969; Banwart and Bremner, 1975; Smith et al., 1977; Yasuhara, 1987). Deibel (1967) found that butyric acid, ethanol, and acetoin were the main volatile components in stored poultry manure. Burnett (1969) found mercaptans, sulfides, and diketones in the headspace of accumulated liquid poultry manure, and volatile fatty acids (VFAs), indole, and skatole in the liquid. Banwart and Bremner (1975) reported that volatile sulphur compounds such as H_2S , methyl mercaptan (MM), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) were

detected from poultry manure under anaerobic conditions. Various alcohols, ketones, esters, and carboxylic acids together with DMS and DMDS were found when poultry manure was incubated in an Ar atmosphere (Smith et al., 1977). Yasuhara (1987) reported 72 compounds identified in poultry manure with a GC-MS. Branched aliphatic alcohols, many esters, dimethyl trisulfide (DMTS) and alkanamides were then detected for the first time. Yasuhara (1987) identified butyric acid, isovaleric acid, DMTS, indole and skatole as the most important odorous components using the odor impact factor defined as the ratio of concentration to the odor detection threshold value.

Several different sampling and sample preparation techniques were used for characterization of the volatile fraction of poultry manure, such as solvent extraction, trap tube (Smith et al., 1977), steam distillation (Deibel, 1967) and freeze vacuum distillation (Yasuhara, 1987). Standard air sampling methods were also modified to quantify VOCs in and around swine operations (Schiffman et al. 2001, Zahn et al. 2001, Blunden et al. 2005). However, caution should be exercised when standard methods are modified for determination of VOCs and semi-VOCs in livestock environments. This is because livestock gases are often polar, reactive, and can interact with each other, moisture in the air, and the sampling container materials (McConnell and Trabue, 2006; Trabue et al., 2006, Trabue et al. 2005, Koziel et al. 2005). The EPA TO-17 method utilizing sorbent tubes and active sampling often used for ambient air sampling was not specifically developed for the compounds of interest in this study, carboxylic acids, sulfides, amides, indolics, phenolics, branched ketones, and high molecular weight aldehydes (Woolfenden and McClenny, 1997). Whole air sampling utilizing evacuated canisters and air sampling bags can be associated with poor sample recoveries for typical malodorous

gases found in livestock environments (Keener et al. 2002; Koziel et al. 2005, Trabue et al., 2006). Some improvement in sample recoveries can be achieved for sulfides with special surface treatments in canisters. However, the presence of moisture appears to lower sample recoveries with storage time (Trabue and Scoggin, 2006).

Solid phase microextraction (SPME) is alternative to conventional sampling techniques such as adsorbent tubes (Koziel, 1999) and offers easy handling, high selectivity and sensitivity for quantitative analysis of airborne compounds (Koziel et al., 2000; Koziel and Pawliszyn, 2001; Augusto et al., 2003). It is specially suitable for qualitative and quantitative analysis of VOCs requiring exposure of a fiber to the headspace above the sample for a suitable period of time, followed by direct thermal desorption in the heated injection port of a GC (Matich, 1999). Quantitative air sampling with SPME can be affected by competitive adsorption, sampling variables such as air velocity and temperature (Jia et al., 2000; Koziel and Pawliszyn, 2001; Koziel et al., 2000). However, air velocity and temperature effects can be minimized when SPME is used as a time-weighted average sampling device (Martos and Pawliszyn, 1999). Competitive adsorption and displacement caused by limited sorption capacity of porous SPME fibers can be minimized by using short sampling times (Jia et al., 2000). The reproducibility of SPME methods was compared with the standard NIOSH method (NIOSH, 1994) showed that the SPME methods generally better than that of the conventional charcoal tube methods (Jia et al., 2000; Koziel and Pawliszyn, 2001) for air samples with target VOCs. Review of air sampling methods utilizing SPME for VOCs in indoor air is presented elsewhere (Koziel and Novak, 2002). To date, limited progress has been made with SPME applications to quantification of odorous gases in and around livestock and poultry operations. SPME has been useful for

qualitative characterization and screening of livestock gases. Sampling of livestock VOCs and odorants with SPME has been used to characterize swine dust odorants (Cai et al., 2006), downwind odor impact of a beef cattle feedlot (Wright et al., 2005), and downwind odor impacts of swine finisher operations (Bulliner et al., 2006; Koziel et al., 2006).

Odors from livestock wastes are due to a complex mixture of volatile compounds arising from anaerobic degradation of plant fiber and protein in the feed (Spoelstra et al., 1980; Hammond et al., 1989). Identification of odorous compounds in livestock wastes is very important to improve the understanding of the potential of malodor generation. Livestock odor results from hundreds of compounds and their possible interactions with each other (Schiffman et al., 2001; Zahn et al., 2001). Wright et al. (2005) demonstrated that SPME combined with a multidimensional GS-MS-Olfactometry (MDGC-MS-O) system can be used for sampling, identification, and prioritization of specific odorants associated with livestock. Although livestock odors are made up of hundreds of compounds (Schiffman et al. 2001), only a handful of compounds are responsible for the characteristic beef cattle and swine odor (Wright et al., 2005) and downwind impact of beef cattle and swine operations (Koziel et al., 2006, Bulliner et al., 2006). Odor reduction for livestock and poultry wastes could be directed towards the most significant characteristic odor-causing components to facilitate development of odor control technologies. Concentrations of key odorous compounds are often very low, e.g., in low ppb range or less. However, odor thresholds of these compounds are even lower. Therefore, suitable sampling/sample preparation and analytical methods are required for the identification of the key odorous compounds.

The objective of this research was to qualitatively evaluate the effectiveness of natural zeolite as a manure additive to control odor and VOCs during simulated laying hen manure storage. The zeolite was topically applied to fresh laying hen manure at a rate of 0, 2.5%, 5% or 10% (by weight). Headspace samples from the storage/emission vessels were collected with SPME 85 μ m Carboxen/PDMS and analyzed on a MDGC-MS-O for the identification and prioritization of poultry manure odorants.

The approach used in this study allowed for qualitative evaluation of odor reduction associated with specific odorants that were separated with GC and identified with MS-O. Measurements of odor concentration with triangular forced-choice olfactometry were not in the scope of this study (ASTM, 2001). This ASTM E697-91 standard method is not suitable for specific odorant identification and prioritization. Parker et al. (2005) reported poor correlations between measured odor concentrations, odor intensity and odor hedonic tones when the triangular forced-choice olfactometry was applied to beef cattle odor. The MDGC-MS-O approach could provide additional information related to the specific odorant identity, odor prioritization and ranking (Wright et al. 2005; Bulliner et al. 2006).

MATERIALS AND METHODS

Emission Apparatus

The emission vessel system has been previously described in detail by Liang et al. (2005). Eight 19-liter (L) emission vessels were operated under positive pressure, with headspace mixing achieved by small 12VDC fans. Fresh air with a constant flow rate of 3 L/min

was introduced into each vessel. The vessels were housed in a laboratory with temperature maintained between 21-25 °C.

Experimental Procedure

Manure Treatment

Nearly fresh hen manure was collected from a commercial belt cage layer facility located in Central Iowa. About 2.5 kg of fresh manure was loaded into a 3.8 L container with 0.02 m² surface area. Different amounts of zeolite (grade 14×40, Bear River Zeolite Company, Thompson Falls, MT) of 0g, 62.5 g, 125 g or 250 g, i.e., 0%, 2.5%, 5%, and 10% by weight, respectively, were surface-applied on top of the manure, corresponding to an application rate of 0, 3.125, 6.25, or 12.5 kg·m⁻² manure surface. Each container was placed inside the 19-L emission vessel. Two vessels were used for each of the dosages. Two trials (Trials A and B) were conducted to achieve four replicates of each treatment. In Trial C, fresh manure (5 cm thickness and 2.5 kg per layer) was loaded to 19-L vessels (as opposed to the smaller 3.8 L container, then placed inside the vessel) every other day for four layers to simulate periodic manure addition and zeolite application to manure storage. Zeolite (125 g, 5% by weight) was surface-applied on top of each layer in four of the eight vessels while the others served as control. Zeolite application rate was equivalent to 2.55 kg·m⁻² manure surface in Trial C. The air exchange rates ranged from 11 to 21 air changes per hour in each vessel as a result of the increasing manure volume from manure addition and decreasing headspace volume.

Sampling and Analysis of VOCs and Odor

Carboxen/PDMS 85 μm SPME fiber (Supelco, Bellefonte, PA) was used for sampling headspace above the poultry manure in the emission vessels. New fibers were conditioned according to the manufacturer's instructions. SPME fiber assemblies had their tensioning spring removed and samples were collected manually. Before each sampling, SPME fibers were desorbed in a GC injector for 5 min at 260 °C, then SPME collections were carried out by direct fiber exposure in the dynamic headspace of the emission vessels for 10 min. The selection of sampling time was based on the preliminary tests of control headspaces with varying SPME sampling times. The 10 min sampling time consistently resulted in detectable amounts of all major odorants and odorous VOCs associated with poultry manure. The effects of limited SPME sorbent capacity were also tested with SPME sampling from static headspaces. No competitive extraction and displacement were observed for all target compounds for sampling up to 10 min, except for methyl mercaptan and dimethyl sulfide.

The headspace SPME sampling was carried out at room temperature and was immediately followed by sample analyses on a MDGC-MS-O system (Microanalytics, Round Rock, TX). The system integrated GC-O with conventional GC-MS (Agilent 6890N GC / 5973 MS, Agilent Inc., Wilmington, DE) as the base platform with the addition of an olfactory port. The system was equipped with a non-polar precolumn and polar analytical 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 (atomic mass units). Spectra were collected at 6 scans/sec and electron multiplier voltage was 1200 to 1350 V. The detector was auto-tuned weekly.

During each trial headspace of all vessels was sampled once only. Two headspace samples (one control and one treatment) were taken on other days. Headspace samples for the same one control and one 10% treatment emission vessel for Trial A were carried out on day 1, day 2, day 3, day 8 and day 9. Problems with the GC motherboard prevented more frequent sampling for this trial between day 3 and day 8. Headspace of all eight vessels were sampled on day 2. For Trial B, headspace of the same one control and one 10% treatment emission vessel were sampled daily between day 1 and 7. For Trial C, headspace of the same one control and one 5% treatment emission vessel were sampled daily between day 1 and 8, and then on day 10, 12, and 14, respectively. Headspace sampling of all eight vessels was performed on day 3 for Trials B and C.

The identity of compounds was verified by combination of (a) high purity reference standards (Sigma-Aldrich, Fisher, and Fluka) and matching their retention time on the MDGC capillary column and mass spectra; (b) matching mass spectra of unknown compounds with BenchTop/PBM (Palisade Mass Spectrometry, Ithaca, NY) MS library search system and spectra of pure compounds, and (c) matching the description of odor character.

Human panelists were used to sniff separated compounds simultaneously with chemical analyses. Odor evaluations consisted of qualitative comparisons of (a) the number of separated odor events and (b) the total odor defined here as sum of the product of odor intensity and odor event duration for all separated odor events recorded in an aromagram (Cai et al., 2006, Bulliner et al., 2006). In this approach, odor intensity and odor character are recorded and measured for

each compound in an air sample causing odor without considering potential odorant interactions. The total odor was not compared with actual odor concentrations. An aromagram was recorded by a panelist utilizing the human nose as a detector. Odor events resulting from separated compounds eluting from the column were characterized for odor descriptor with a 64-descriptor panel and odor intensity with Aromatrx software (Microanalytics, Round Rock, TX). The olfactory responses of a panelist were recorded using Aromatrx software by applying an odor tag to a peak or a region of the chromatographic separation. The odor tag consisted of editable odor character descriptors, an odor event time span (odor duration) and perceived odor intensity. The relative % reduction was used to evaluate the effectiveness of different zeolite application rates. Relative amount of volatiles present in the headspace above the manure was measured as peak area counts under peaks of characteristic single ions for separated gases. Treatment effectiveness of specific VOCs and potential odor control measured with the GC-O approach was expressed as percent reduction, i.e., as the ratio of the difference between the control and treatment to the control, of the form:

$$\% \text{Reduction} = \frac{C_i - T_i}{C_i} \times 100\% \quad [1]$$

where:

C_i = peak area count of compound or odor “i” for the control hen manure, and

T_i = peak area count of compound or odor “i” for the zeolite-treated hen manure.

Positive value of % reduction means the zeolite treatment was effective for that particular compound. Negative numbers signify that the treatment was not effective, i.e., treatment generated a particular compound instead of reducing it. The relative reduction did not refer to specific concentrations.

Reproducibility of HS-SPME method for VOCs emitted from poultry manure

Reproducibility of the method expressed as relative standard deviation (RSD) for 24 target VOCs typically present in the headspace of poultry manure was tested. Five replicates samples were collected at room temperature from the headspace of the same control vessel using the same 85 μm Carboxen/PDMS fiber and 10 min extraction time, followed with analysis on a GC-MS. The RSD ranged from 2.0% to 28.3 % for all 24 target compounds with the exception of phenol (44.9%). Average RSD was 12.7%. Values of RSD ranged from 5.2 to 12.8% for aldehydes, 9.1 to 12.5% for VFAs, 6.4 to 44.9% for phenolics, 10.6 to 13.0% for indolics and 2.0 to 19.7% for sulfide compounds.

RESULTS and DISCUSSION

Effects of zeolite application rates on VOCs

A total of more than 90 volatile compounds were identified from the headspace air. Among those compounds only several chemical groups contributed to the offensive odor of poultry manure, including short-chain VFAs, volatile sulfur compounds, phenolic and indolic compounds. Eight characteristic compounds which significantly contribute to the malodor of poultry manure, including butanoic acid, isovaleric acid, DMTS, dimethyl sulfone, phenol, indole and skatole, were selected for comparisons of the effect of zeolite application rates. Effects of the three application rates of the natural zeolite on target VOCs are shown in Table 1. Data in Table 1 represent the reduction (%) for different zeolite application rate (2.5%, 5% and 10%, by weight) of target odorants and characteristic odors for Trial A and B evaluated with GC-MS-O. Close inspection of the data in Table 1 shows that acetic acid, butanoic acid, isovaleric acid, indole and skatole were controlled by zeolite application. The reduction of those

compounds and its statistical significance was generally proportional to the zeolite application rate. However, DMTS and phenol were generated, and the rate of generation was proportional to the application rate, except for phenol at 10% application rate.

Six characteristic odors present in the poultry manure were then selected to further evaluate the effects of zeolite application rates on odor impact (Table 1). The odor shown in Table 1 was defined as the product of odor intensity (%) and odor duration (min) for each characteristic odor recorded in aromagram (Cai et al, 2006). Six characteristic odors were correlated with corresponding compounds, i.e., ‘onion/garlic’ (DMTS), ‘fatty acid/body odor’ (butanoic acid), ‘body odor’ (isovaleric acid), ‘phenolic’ (phenol), ‘barnyard’ (indole), and ‘naphthalenic’ (skatole). Apparent reduction in odor caused by VFAs, skatole and indole was consistent with the chemical analyses shown in Table 1. Similarly, the reduction of odor was typically proportional to the rate of application. The odor intensity from acetic acid was much smaller compared with the six characteristic compounds. The ‘vinegar, acidic’ odor character for acetic acid is also less offensive compared with higher molecular weight fatty acids. Thus, acetic acid is not shown in Table 1. Among the dosages tested, 10% zeolite was the most effective in controlling VOCs and odors emitted from poultry manure as evaluated with the GC-MS-O approach.

Comparing Average Effectiveness of 10% Zeolite Treatment for Trials A and B

Thirty compounds belonging to seven chemical groups, such as ketone (2), aldehyde (3), VFAs (6), phenolic (5), indolic (2), N-containing compounds (5) and S-containing compounds (7),

were selected to evaluate the effectiveness of a 10% zeolite treatment. Figure 1 shows comparison of total ion chromatograms (TICs) of 10% zeolite treatment and control. Table 2 summarizes the comparison of the average effectiveness of 10% zeolite treatment for each of the target 30 compounds for Trials A and B. Twenty two out of 30 compounds including 2 ketones, benzaldehyde, 6 VFAs, 4 phenolics, 2 indolics, 5 N-containing compounds and 2 S-containing compounds were consistently controlled in Trials A and B. However, some sulfur compounds, such as MM, DMS, DMDS, 1-propanethiol and especially DMTS, were generated over time in both trials. A possible reason is that zeolite changed the pH of poultry manure and resulted in the generation of sulfur compounds. Also, sulfur compounds could have been generated because the surface-applied zeolite layer could facilitate formation of anaerobic condition in the manure. Banwart and Bremner (1975) reported that volatile sulfide compounds such as H₂S, MM, DMS, and DMDS were emitted from poultry manure under anaerobic conditions. Some authors reported apparent sulfur compound generation associated with the use of Carboxen/PDMS fiber coatings, also known to be the most suitable fiber for analyzing sulfur compounds (Lestremau et al., 2004). This fiber coating is known for artifact DMDS formation of as much as 25% (Lestremau et al., 2004). Carboxen coatings contain between 1 and 4% of sulfur material (Dettmer and Englewald, 2002). In this study, the possible artifact formation should be offset (and not affect the % reduction estimates) by qualitative comparisons of treatment and control and the used of equation [1]. Phenol is the only compound generated in Trial A and controlled in Trial B. Analysis of headspace of only the zeolite material used in this study showed that phenol was emitted from zeolite. Thus, the variability of treatment/generation observed for phenol might be attributed to its presence in zeolite.

The average treatment effectiveness evaluated with SPME-GC-O approach for seven chemical groups in both trials were 47% for ketones, 23% for aldehydes, 89% for VFAs, 57% for phenolics except for phenol, 77% for indolics, 98% for amines, 42% for sulfur-oxidation compounds, -532% for sulfides, respectively. Statistical analyses were carried out using paired *t* test to detect the significance of observed difference. The control of acetic acid, skatole and dimethyl sulfone was significant ($p < 0.05$) for 10% zeolite treatment in both Trials A and B. Few compounds were significantly reduced in one of the trials only. In Trial A, 3-octanone and propanamide were significantly ($p < 0.05$) controlled. In Trial B, propanoic, isobutyric, butanoic, isovaleric, pentanoic acids, phenol, *p*-cresol, 4-ethyl phenol, 4-vinyl phenol, guaiacol, indole, skatole, acetamide, propanamide, 2-methyl- propanamide, butanamide, and trimethyl amine were controlled ($p < 0.05$). MM, DMS, and 1-propanethiol were generated ($p < 0.05$). However, 23 out of 30 target odorous compounds showed significant difference ($p < 0.05$) between control and treatment for pooled trial A and B (Table 2). The average standard deviations of removal means for all selected compounds except for DMTS in both trials were calculated. The average standard deviation (except for DMTS) of Trial A was greater than that of Trial B (48% vs. 25%). The variability is likely due to the degradation of manure and/or SPME sampling without septa causing the concentration of the headspace changing, as well as possible variations in extraction efficiency for different SPME fibers.

Figure 2 (A and B) show the effectiveness of 10% zeolite application rate treatment for five representative compounds over time for Trials A and B. Trimethyl amine, acetic acid, skatole, indole and DMTS were selected for evaluation of the effectiveness. For all the selected compounds, the effectiveness changed over time. However, different compound showed

different changing trends, i.e., upward trend (acetic acid), downward trend (indole and skatole), consistent trend (trimethyl amine and DMTS), respectively.

The percentage reduction of specific compounds reported in this paper is based on qualitative evaluations according to equation [1] without estimating actual compound concentrations. However, it could be assumed that percentage reduction estimated with this qualitative approach is not significantly different from the percentage reduction that would be obtained if % reduction was estimated based on estimates of concentrations. This is because no significant effects of competitive adsorption were observed on the SPME fiber coatings used for the same sampling time and sampling temperature. Potential biases associated with selective extractions and the use of different SPME fibers (Jia et al, 2000) should also be relatively insignificant when equation is used for qualitative comparisons. More research is warranted to test these assumptions with suitable air sampling and analysis methods.

Comparison of total odor and odor events between 10% zeolite treatment and control

Figures 3 A and B show the comparison of total odor and odor events between 10% zeolite treatment and control in Trials A and B. The total odor was estimated as the summation of the products of odor duration and odor intensity for all odor events found in all headspace samples of poultry manure. Total odor from the control was always higher than that from the 10% zeolite treatment over time in both trials. The total odor for trial A and B showed significant difference ($p = 0.0016$) between control and treatment. Average reduction of the odor caused by all odorants evaluated with SPME-GC-O was 67% ($\pm 12\%$) and 51% ($\pm 26\%$) for Trials A and B,

respectively. The same trend was observed for the total number of odor events. The apparent reduction in the estimate of odor and the total number of odors detected was consistent for both trials. Thus, the overall odor in poultry manure appeared to be controlled by 10% zeolite application. Average reduction of the total odor evaluated with SPME-GC-O approach for 2.5%, 5%, and 10% treatment was 33%, 50%, and 83% for Trial A, and -29%, 3%, and 55% for Trial B, respectively, when headspace of all treatments was compared. This apparent correlation between the loading rate and the reduction of the total odor is consistent with the similar trend observed for several target VOCs. It is interesting to mention that the effectiveness of zeolite treatment in the 7-day cumulative ammonia emission for 2.5%, 5% and 10% treatment were 68%, 81% and 96% of control, respectively. The effectiveness of ammonia reduction decreased as storage time went by, possibly due to its decreased capacity (Liang et al., 2005). The better performance of zeolite in controlling ammonia emission from poultry manure storage might be associated with its natural selectivity for ammonia by zeolite.

Comparing average effectiveness of 5% zeolite treatment for Trial C

In Trial C, 5% zeolite application rate was surface-applied on top of each manure layer (zeolite addition interval of 2 days, 4 layers in total). This was done in an attempt to simulate manure collection and treatment in a typical layer barn with belt manure removal and storage. The evaluation of the effects of zeolite application simulating periodic application is displayed in Table 3. Twenty two compounds were selected to evaluate the effectiveness of zeolite treatment using equation 1. Only trimethyl amine was controlled over the 14-day trial duration. Skatole and diacetyl were randomly controlled. Average treatment effectiveness for the remaining

compounds was negative. Figure 4 shows comparison of total odor area count between treatment and control. Total odors evaluated with the SPME-GC-O approach on days 1, 2, 3, 5, 8 and 12 in treatment were higher than that in control. The total odor for trial C showed no significant difference ($p=0.1439$) between control and treatment. Average reduction of the total odor was actually negative (-9%) (St.dev. $\pm 21\%$). These results indicated that there were no apparent odor and VOCs control with the layered 5% zeolite application. However, there were three compounds, i.e., trimethyl amine, dimethyl trisulfide and skatole which showed significant difference ($p<0.05$) (Table 3). It is noteworthy that fresh manure was loaded directly into the 19L vessel with 0.05 m^2 manure surface in Trial C (as opposed to the smaller 3.8 L container in Trials A and B). Zeolite application rate was equivalent to $2.55 \text{ kg}\cdot\text{m}^{-2}$ manure surface for 5% application rate, which was much less than the equivalent $6.25 \text{ kg}\cdot\text{m}^{-2}$ (5% by weight) rate in Trials A and B. Hence, the total zeolite adsorption capacity in trial C was presumably much lower than that in Trials A and B.

Caution should be exercised when interpreting qualitative odor comparisons in this study. The total odor was defined here as sum of the product of odor intensity and odor event duration for all separated odor events recorded in an aromagram for each air sample (Cai et al., 2006, Bulliner et al., 2006). In this approach, odor intensity and odor character were recorded and measured for each compound in an air sample causing odor without considering potential compound interactions and its potential effect on odor concentrations. This approach is useful in determination of specific compound or compounds causing specific odors in complex air samples associated with livestock odor (Wright et al., 2005). The total odor was not compared

with actual odor concentrations. Research is warranted to determine the effect of individual odorous compounds typically found in livestock odor on measured odor concentrations.

CONCLUSIONS

The following conclusions were drawn from this study:

- Sampling with SPME and analysis with GC-MS-O is a useful qualitative approach for testing of treatment effectiveness of zeolite applications to control VOCs and specific odorants from simulated poultry manure storage.
- Topical application of zeolite to laying hen manure showed the potential for reducing emissions of acetic acid, butanoic acid, isovaleric acid, dimethyl sulfone, phenol, indole and skatole from the manure storage, with the effectiveness of treatment being proportional to the zeolite application rate.
- Sulfide compounds including DMS, DMDS, DMTS, MM, 1-propanethiol were generated with the rate of generation being generally proportional to the application rate.
- Specific odors caused by VFAs, skatole and indole, i.e. fatty acid/body odor (butanoic acid), body odor (isovaleric acid), barnyard (indole), and naphthalenic (skatole) were controlled by 10% topical zeolite treatment.
- 10% zeolite application rate is the most effective on controlling specific odorants emitted from poultry manure among the tested application rates. Average reduction of the total odor measured with the GC-O approach was 67% ($\pm 12\%$) and 51% ($\pm 26\%$) for Trials A and B, respectively.

ACKNOWLEDGEMENTS

This research was funded in part by the Women in Science and Engineering Program at the Iowa State University, the Midwest Poultry Research Program, and a Special USDA-CSREES Air Quality Research Grant.

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FIGURE CAPTIONS

Figure 1 Comparison of total ion chromatogram (TIC) between 10% zeolite treatment and control.

Figure 2 Effects of 10% zeolite treatment on characteristic compounds emitted from manure over time for Trial A (part A) and Trial B (part B).

Figure 3 Effects of 10% zeolite treatment on the total odor evaluated with GC-O for Trial A (part A) and Trial B (part B). Total odor was defined as the sum of all separated odor peak areas (product of separated odor intensity and odor duration on an aromagram).

Figure 4 Effects of four layer 5% zeolite treatment on the total odor evaluated with GC-O for Trial C.

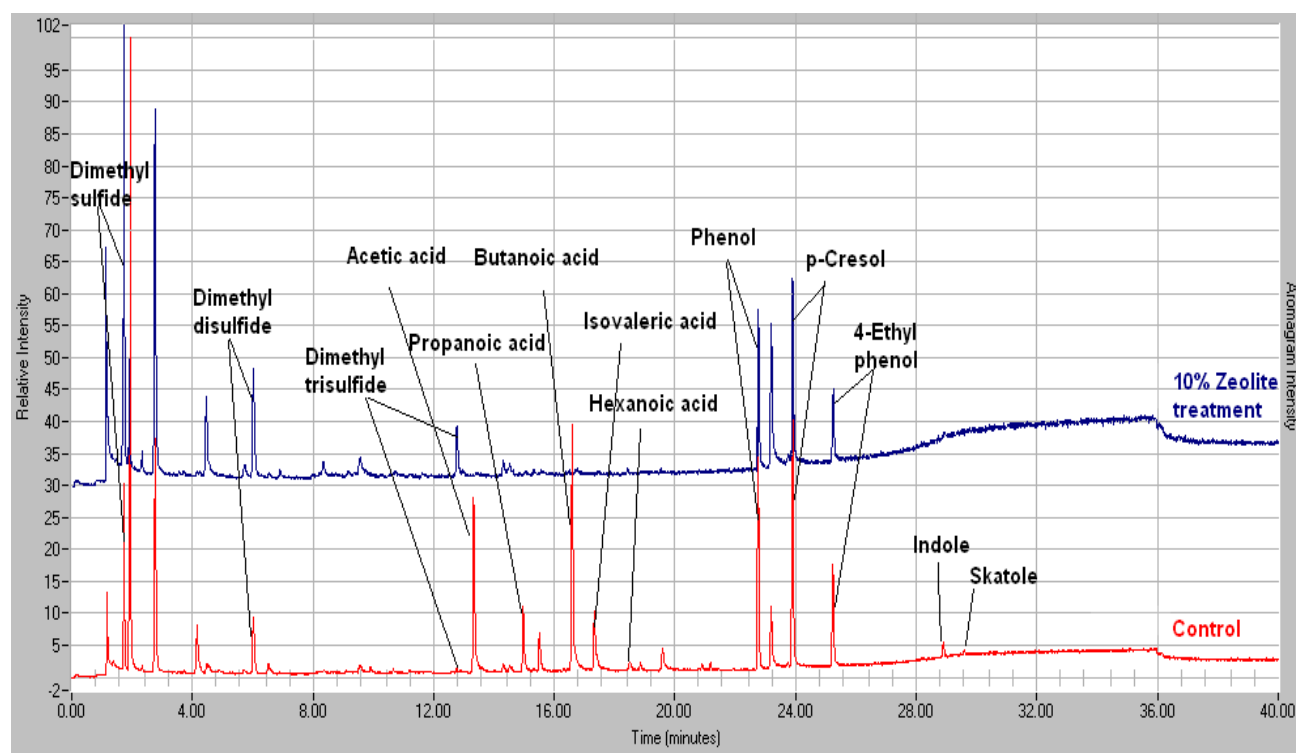


Figure 1 (Cai et al.)

(note – this figure could be published without color)

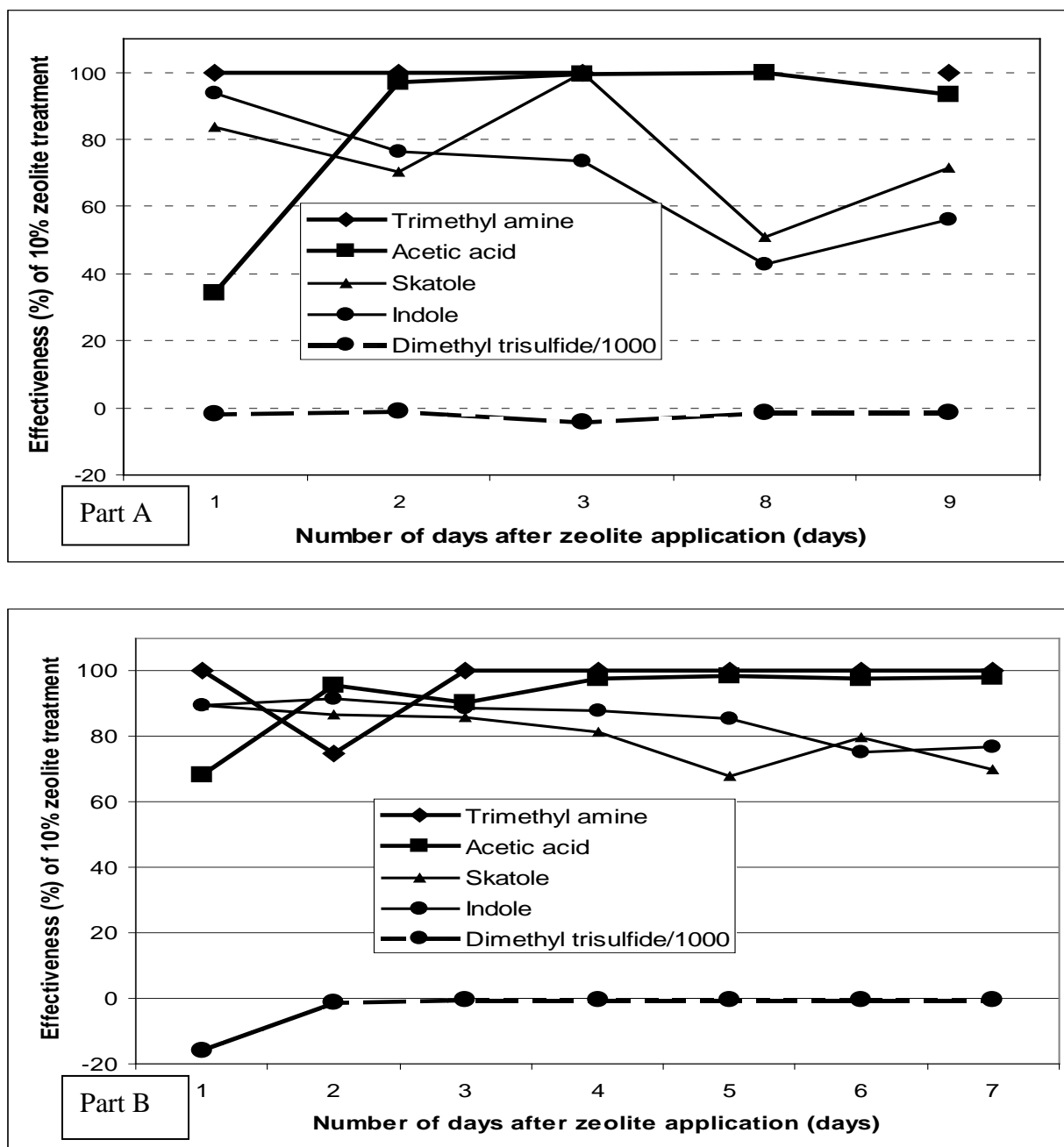


Figure 2 (Cai et al.)

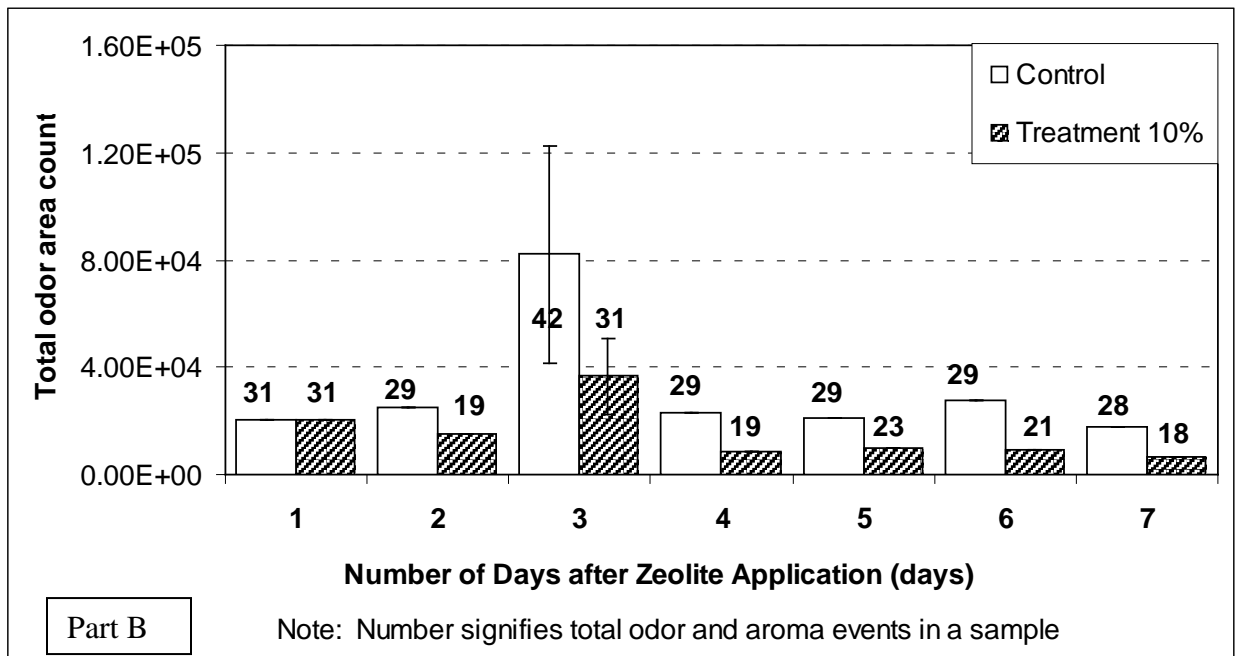
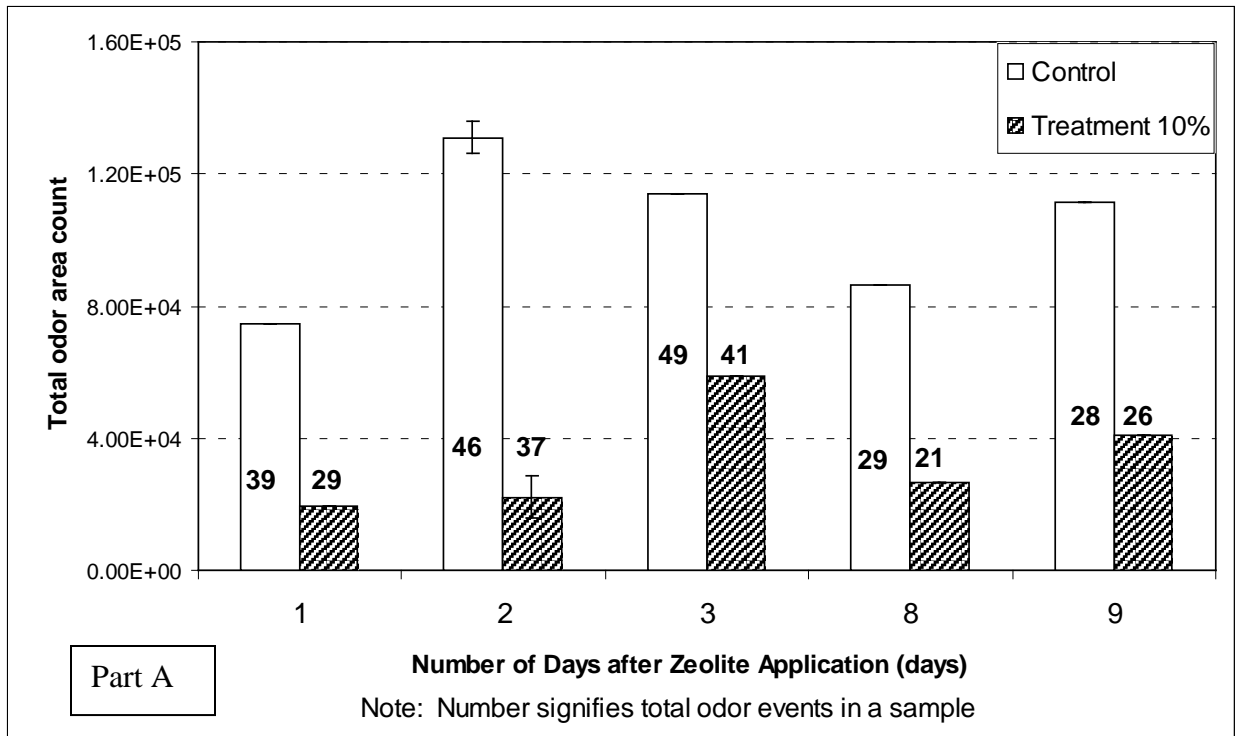


Figure 3 (Cai et al.)

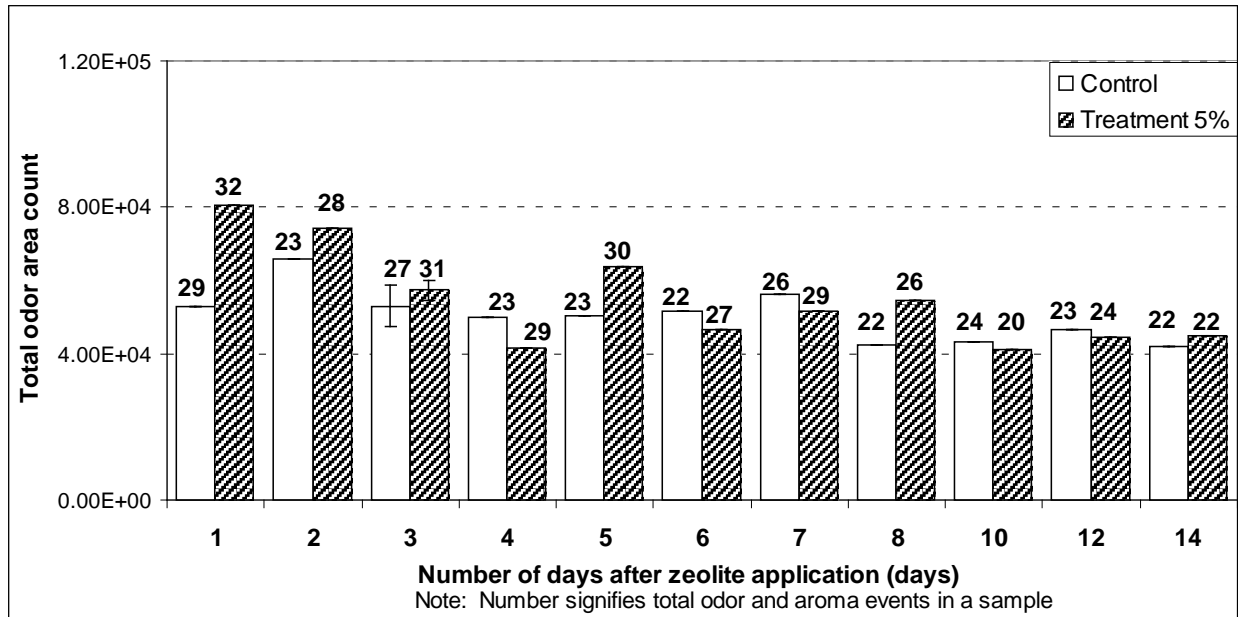


Figure 4 (Cai et al.)

Table 1. Reduction (%) of different zeolite application rate (2.5%, 5% and 10%, by weight) on target odorants and characteristic odors for Trial A and B evaluated with GC-MS-O.

Compound Name	Zeolite application rate by weight								
	2.5%			5%			10%		
	Trial A	Trial B	p value (t test for A&B)	Trial A	Trial B	p value (t test for A&B)	Trial A	Trial B	p value (t test for A&B)
Dimethyl trisulfide	-137	-17	0.2841	-551	-187	0.1597	-556	-821	0.0626
Acetic acid	66	-578	0.4910	89	-161	0.6833	96	82	0.0614
Butanoic acid	47	-436	0.2535	81	7	0.1075	96	97	0.0457
iso-Valeric acid	59	-327	0.2204	84	51	0.0210	100	100	0.0344
Dimethyl sulfone	-3	-15	0.3524	57	45	0.0046	94	74	0.0051
Phenol	-250	-6	0.3336	-478	-100	0.0435	-259	-113	0.0149
Indole	-3	36	0.5893	26	61	0.2716	82	77	0.0684
Skatole	24	36	0.0690	53	42	0.0741	72	75	0.0187
Odor (Compound)									
'Onion' (dimethyl trisulfide)	38	12	0.1613	-134	-64	0.1427	-98	-18	0.1443
'Fatty acid' (butanoic acid)	92	-767	0.6536	73	-480	0.7730	97	100	0.3038
'Body odor' (isovaleric acid)	75	-141	0.7973	98	15	0.1513	96	90	0.0582
'Phenolic' (phenol)	64	100	0.3698	11	100	0.3414	86	100	0.2658
'Barnyard' (indole)	-150	-69	0.1448	-135	-39	0.1634	55	31	0.1367
'Naphthalenic' (skatole)	75	-132	0.8613	89	-43	0.4126	98	60	0.0718

Table 2. Qualitative comparison of average reduction (%) estimated with equation [1] of 10% zeolite treatment for entire Trial A and Trial B. Number in parentheses is the single ion of each compound used for peak area count integration.

Compound name	RT (min)	Trial A			Trial B			Trial A&B		
		% Reduction	St. Dev.	<i>p</i> -value (<i>t</i> test)	% Reduction	St. Dev.	<i>p</i> -value (<i>t</i> test)	% Reduction	St. Dev.	<i>p</i> -value (<i>t</i> test)
<i>Ketones</i>										
Diacetyl (86)	3.68	41	38	0.2655	7	102	0.0691	21	81	0.0324
3-Octanone (99)	10.97	84	11	0.0467	54	30	0.0828	65	29	0.0065
<i>Aldehydes</i>										
Hexanal (56)	6.45	38	68	0.1355	-	-	-	16	45	0.1355
Heptanal (70)	9.05	48	34	0.2224	-	-	-	11	24	0.2224
Benzaldehyde (106)	14.93	47	37	0.1972	1	45	0.7645	20	46	0.1817
<i>VFAs</i>										
Acetic acid (60)	13.30	85	28	0.0283	92	11	0.0230	89	19	0.0014
Propanoic acid (74)	14.95	87	24	0.1416	89	21	0.0255	88	21	0.0182
Isobutyric acid (73)	15.48	53	78	0.1196	100	0	0.0114	100	0	0.0113
Butanoic acid (60)	16.60	75	49	0.0883	94	15	0.0158	86	33	0.0134
Isovaleric acid (60)	17.30	100	0	0.1218	100	0	0.0203	100	0	0.0117
Pentanoic acid (60)	18.46	97	5	0.1399	100	0	0.0127	89	31	0.0086
<i>Phenolics</i>										
Phenol (94)	22.75	-104	261	0.6430	55	26	0.0041	-16	177	0.0205
<i>p</i> -Cresol (107)	23.87	12	48	0.4530	73	12	0.0006	48	44	0.0031
4-Ethyl phenol (107)	25.22	56	34	0.1334	57	26	0.0125	57	28	0.0022
4-Vinylphenol (120)	28.08	62	50	0.1928	43	24	0.0023	51	36	0.0630
Guaiacol (124)	20.58	83	6	0.1703	93	13	0.0017	90	12	0.0115
<i>Indolics</i>										
Indole (117)	28.82	68	20	0.1479	85	6	0.0083	78	15	0.0018
Skatole (130)	29.50	75	18	0.0066	80	8	0.0037	78	13	0.0002
<i>N-containing compounds</i>										
Acetamide (44)	18.78	89	20	0.1155	100	0	0.0006	77	42	0.0009
2-Methyl propanamide (59)	19.48	100	0	0.3910	100	0	0.0015	78	44	0.0084
Propanamide (57)	19.55	93	10	0.0095	100	0	0.0133	87	33	0.0053
Butanamide (72)	20.81	98	2	0.1090	100	0	0.0018	77	44	0.0007
Trimethyl amine (58)	1.28	100	0	0.0703	96	9	0.0202	98	8	0.0016
<i>S-containing compounds</i>										
Methyl mercaptan (47)	1.38	-40	53	0.1841	-70	68	0.0333	-58	62	0.0765
Dimethyl sulfide (62)	1.63	-100	146	0.1631	-70	41	0.0065	-82	94	0.0041
1-Propanethiol (76)	2.20	-122	111	0.0567	-96	50	0.0072	-107	78	0.0005
Dimethyl disulfide (79)	5.85	-46	163	0.6057	-44	119	0.4433	-45	132	0.7972
Dimethyl trisulfide (126)	12.60	-1935	1310	0.0936	-2795	5813	0.1250	-2437	4388	0.0155
Dimethyl sulfoxide (63)	15.42	21	61	0.2567	24	41	0.3335	23	48	0.1461
Dimethyl sulfone (79)	21.11	95	6	0.0073	87	10	0.0014	90	9	0.0000

% reduction estimated with equation [1].

1 Table 3. Reduction (%) of 4-layer treatment for Trial C estimated with equation [1]. Number in parentheses is the single
 2 ion of each compound used for peak area count integration.

Compound name	RT (min)	Layer 1		Layer 2		Layer 3		Layer 4					Average		
		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8	Day 10	Day 12	Day 14	AVG	ST. DEV.	p-value (t test)
Ketones															
Diacetyl (86)	3.68	-41	-28	15	3	-26	-39	8	30	16	36	26	0	28	0.8385
3-Octanone (99)	10.97	-17	-23	-13	-10	-121	-61	53	50	34	17	41	-5	53	0.9016
Aldehydes															
Benzaldehyde (106)	14.93	-302	-686	-67	-195	-97	-71	13	-30	-46	-48	-46	-143	200	0.0554
VFAs															
Acetic acid (60)	13.30	-55	-481	-51	-378	36	40	12	-102	-155	-187	20	-118	173	0.0964
Propanoic acid (74)	14.95	-165	-923	-73	-579	8	37	-25	-167	-37	-171	-102	-200	292	0.0691
Butanoic acid (60)	16.60	-322	-774	-315	-1,032	-106	-6	54	-99	-73	-296	-10	-271	343	0.0536
Isobutyric acid (73)	15.48	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	n/d	-81	-81	-
Phenolics															
4-Ethyl phenol (107)	25.22	2	-27	-5	-57	-6	25	58	-48	-90	-91	-118	-32	54	0.4152
Phenol (94)	22.75	8	-153	-261	-194	-63	-36	-2	-25	15	38	47	-57	102	0.6956
4-Vinylphenol (120)	28.08	-28	-39	-11	-21	11	14	62	-11	-28	-33	-23	-10	29	0.1527
p-Cresol (107)	23.87	-4	-124	-187	-331	-47	-94	30	-195	-205	-136	-101	-127	102	0.3127
Guaiacol (124)	20.58	-25	-65	-49	-66	-1	-2	18	-50	66	53	79	-4	53	0.9915
Indolics															
Indole (117)	28.82	56	16	1	-44	37	14	18	-74	-31	-40	-89	-12	46	0.4392
Skatole (130)	29.50	24	11	29	12	23	41	55	40	5	-8	-16	20	22	0.0004
Amines															
Trimethyl amine (58)	1.28	79	67	51	90	96	78	-	82	56	38	52	69	19	0.0419
Sulfides															
Dimethyl sulfone (79)	21.11	-82	-61	-15	-28	1	35	50	18	-18	-17	-2	-11	39	0.2840
Methyl mercaptan (47)	1.38	19	0	9	-11	-101	-47	-1	8	-14	6	13	-11	35	0.6625
Dimethyl sulfoxide (63)	15.42	-63	-38	-30	17	-113	-12	-44	35	10	15	68	-14	50	0.1385
Dimethyl sulfide (62)	1.63	9	-3	12	5	-127	-99	9	3	1	11	-5	-17	48	0.4796
1-Propanethiol (76)	2.20	-26	-14	-7	-21	-184	-77	16	17	-8	14	8	-26	59	0.2840
Dimethyl disulfide (79)	5.85	-34	-144	-38	-17	-243	-340	4	28	32	35	33	-62	126	0.3793
Dimethyl trisulfide (126)	12.60	-162	-314	-116	-153	-272	-201	15	-39	-54	-72	-35	-128	104	0.0086

3 n/d=not detected