PERFORMANCE EVALUATION OF A WOOD CHIP-BASED BIOFILTER USING SOLID-PHASE MICROEXTRACTION AND GAS CHROMATOGRAPHY-MASS SPECTROMETRY-OLFACTOMETRY

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Abstract

A pilot-scale mobile biofilter was developed where two types of wood chips (western cedar and 2 inch hardwood) were examined to treat odor emissions from a deep-pit swine finishing facility in central Iowa. The biofilters were operated continuously for 13 weeks at different air flow rates resulting in a variable empty bed residence time (EBRT) from 1.6 to 7.3 seconds. During this test period, solid-phase microextraction (SPME) PDMS/DVB 65 μm fibers were used to extract volatile organic compounds (VOCs) from both the control plenum and biofilter treatments. Analyses of VOCs were carried out using a

multidimentional gas chromatography-mass spectrometry-olfactometry (MDGC-MS-O) system. Results indicated that both types of chips achieved significant reductions in p-cresol, phenol, indole and skatole which represent some of the most odorous and odor-defining compounds known for swine facilities. The results also showed that maintaining proper moisture content is critical to the success of wood chip-based biofilters and that this factor is more important than media depth and residence time.

1. Introduction

The reduction of odors emitted from livestock and poultry production systems represents a significant challenge for researchers. Biofiltration is a versatile odor and gas treatment technology that has gained much acceptance in agriculture. Several research studies using compost-based biofilters have been conducted with significant reductions in odor and specific gases reported. Nicolai and Janni (1997) reported a compost/bean straw biofilter that achieved average odor and H_2S removal efficiencies of 75% to 90%, respectively. Sun et al. (2000) observed an average H_2S removal efficiency between 92.8% and 94.2%, and an average NH_3 removal efficiency between 90.3% and 75.8% with 50% media moisture content and 20 s gas retention time. Martinec et al. (2001) also found from several biofilter research experiments an odor reduction efficiency up to 95%. The mixture of wood chips and compost (75:25 to 50:50 percent by weight) has been recommended as biofilter media (Nicolai and Janni 2001a). However, the mixture media can cause a high air flow resistance that must be overcome, often with the use of large expensive fans (Devinny et al., 1999; Garlinski and Danny, 2003) which in turn results in excessive electrical energy use. A wood chip-based biofilter can reduce the pressure drop but little is known about the performance of wood chip-based biofilters on reduction of malodor and VOCs emitted from swine facilities.

Most odor and gas emission from building and manure storage sources are by-products of anaerobic decomposition and transformation of organic matter in

manure by microorganisms. The by-products of decomposing animal manure include many volatile compounds (Nicolai, et al. 2006). Kreis (1978) listed 50 compounds in swine manure. O'Neil and Phillips (1992) expanded the list by identifying 168 compounds in swine and poultry manure. Curtis (1983) also reported on principal odorous compounds including ammonia, amines, hydrogen sulfide, volatile fatty acid, indoles, skatole, phenols, mercaptans, alcohols, and carbonyls. Recently, Lo et al. (2008) identified 294 compounds emitted from swine manure by using solid-phase microextraction (SPME) and multidimentional gas chromatography-mass spectrometry-olfactometry (MDGC-MS-O). SPME coupled with MDGC-MS-O is a novel approach to be used for air sampling and simultaneous chemical and olfactory analysis of odor- causing compounds associated with livestock operations. This approach was used to determine the key compounds responsible for the characteristic swine odor at the source (Bulliner et al., 2006), downwind (Koziel et al., 2006) and odor-particulate matter interactions (Cai et al., 2006). Thus, odor mitigation efforts could be directed towards the most significant characteristic odor-causing compounds. Cai et al. (2007) used SPME and GC-MS-O to evaluate the effectiveness of topical zeolite applications to mitigate VOCs and odor from simulated poultry manure storage.

To date, studies have mainly focused on NH_3 and H_2S reductions when evaluating biofilters. More studies are needed to better understand the biofilter's effects on VOCs, especially the principal odorous compounds identified above. Therefore, the objective of this research was to investigate the fate of selected chemicals when subjected to two distinct wood chip-based biofilters operating at

various moisture content and empty bed residence time (EBRT), defined as the volume of the biofilter media divided by the air flow rate passing through the media.

2. Materials and methods

2.1. Experiment site

This research project was conducted at a 1,000-head curtain-sided deep-pit swine finishing facility located in central Iowa. This research was conducted from July 14 to October 13, 2006. The building monitored was approximately 14×55 m with 25 cm and 61 cm diameter fans pulling pit-gases from the pump-out locations.

2.2. Mobile Pilot-Scale Biofilter System

A novel pilot-scale mobile biofilter system, which consisted of a biofilter testing laboratory and a biofilter monitoring laboratory, was constructed for this research project. The mobile testing laboratory was covered at the top and sides to eliminate wind and rain effects on the biofilters being tested. Meanwhile, the mobile monitoring laboratory was used to house all instrumentation hardware and calibration gases required. The set-up is shown in Figure 1a. The layout of the biofilter testing laboratory is shown in figure 1b. The mobile monitoring

laboratory was used to collect all data associated with this project such as temperature, biofilter moisture content, wind speed, wind direction, NH_3 and H_2S concentration.

On the biofilter testing laboratory (Figures 2a,b), there were eight parallel plastic reactor barrels, four of which were randomly selected to be filled with western cedar (WC) chips and the remaining four filled with 5 cm (2 in) hardwood (HW) chips (Figure 2c). There was a common plenum underneath the barrels directly connected to a fan from one of the pump-out locations. Eight adjustable fans (model AXC 100b; Continental Fan Manufacturing, Buffalo, New York) and 10 cm (4 in) PVC pipes were used to connect the common plenum with the eight barrels. In order to homogenize the exhaust air in the plenum, a small fan (model 4C442; Dayton Fans) was installed inside the plenum for mixing purposes.

The reactor barrels (56 cm diameter, 86 cm in depth) were designed with a 25 cm air space at the bottom of the barrel, with the biofilter media located above this airspace, separated by a metal mesh support (Figure 3). Preliminary laboratory tests conducted on seven various chip-based media indicated that WC chips and standard 5 cm (2 in) HW chips were superior based on moisture retention. The decision was then made to test these two products as the media for the pilot-scale biofilters. The WC and HW media porosity was 67.0%±0.5% and 55.9%±0.5% respectively, using the bucket test method (Nicolai and Janni, 2001a). Each of the eight reactors was initially filled to a depth of 51 cm. Water was added manually *via* a spray nozzle at the top of each barrel. Biofilter media moisture was measured with commercially available soil moisture sensors

(model ECH2O EC-20; Decagon Devices, Inc., Pullman, WA) which were first calibrated in the laboratory. Each of the eight reactors had its own variable speed fan that was manually adjusted based on the demands of the experimental design. The variable speed fans were used to adjust EBRT.to 1.6, 2.5, 2.6, 3.3, 3.6, 4.0, 5.3, 5.5, and 7.3 seconds.

2.3. Biofilter operation

The biofilter media in each reactor was allowed to stabilize by passing pit-gas air through each reactor with the media at an initial depth of 51 cm, a maintained moisture content in the 50~60% range (wet basis) and at an air flow rate of 2,265 L/minute. The stabilization period was for a month during which SPME fiber selection and time series test were conducted. After the one month-long stabilization period, the media depth was changed from 51 cm to 38 cm and then to 25 cm over a period of nine weeks, in three week increments. At each depth tested, three levels of air flow rate (2,265 L/minute, 1,410 L/minute and 1,025 L/minute) were randomly set to run in each reactor for about one week during which SPME samples were collected and analyzed. At the final period of this project where the media depth was 25 cm, SPME samples were collected at three different media moisture levels (60%, 40%, 20% wet basis) with a fixed air flow rate of 2,265 L/minute.

2.4. SPME sampling

The SPME sampling system consisted of a funnel, PFA 6 mm (¼ inch) inside diameter Teflon tubing, a 47 mm diameter membrane filter with a 0.45μm pore size, a custom-built PTFE (Teflon) sampling port for the collection of air samples with SPME and a vacuum pump (Figure 3). All sample tubing was heated to prevent condensation within the tubes. The SPME sampling ports were cleaned and dried at 110 ºC overnight before installing. When the SPME samples were collected, the SPME fibers were placed into the customized SPME sampling ports which allowed to expose the fiber to the sample air. Five commercially available fibers including 85 μm Car/PDMS, 65 μm PDMS/DVB, 50/30 μm DVB/Car/PDMS, 85 μm PA and 100 μm PDMS (Supelco, Bellefonte, PA) were first tested to select the most suitable (i.e., efficient in collecting typical swine odorants, Lo et al., 2008) SPME coating for extracting VOCs associated with the pit-gas exhaust air. Before use, each fiber was conditioned in a heated GC splitless injection port under helium flow according to the manufacturer's instructions. SPME sampling time was varied from 10 seconds to 2 hours to determine the optimal SPME sampling time. The system was first allowed to run for 2 minutes to equilibrate and then a SPME fiber was placed into the sampling port where the SPME fiber was exposed in the sample air for the preset sampling time. The fibers were then removed from the sampling port, wrapped in clean aluminum foil and stored in a cooler for transfer to the on-campus laboratory for analysis. All SPME samples were analyzed within 48 hours of collection. The desorption time of SPME fibers in GC injector was always 40 minutes at 260 ºC.

Solid phase microextraction eliminates the use of sample containers and solvents and it combines sampling and sampling preparation into one step. Air sampling with SPME presents many advantages over conventional sampling methods (Koziel et al., 2005; Koziel and Pawliszyn, 2001)] due to its simplicity, reusability, very good sample recovery and hydrophobic property of SPME coatings. Koziel et al (2005) reported average 105% (±11.4%) recoveries of gaseous VFAs (from acetic to hexanoic acid) at room temperature and 24 hrs storage time from the 75 μm Carboxen/PDMS SPME fiber coatings. The variability (measured as standard deviation) for recoveries of VFAs were as low as 2.0%, 3.6%, 9.7%, and 5.6% for propanoic, butanoic, pentanoic, and hexanoic acids, respectively.

[1] .

2.5. Analytical methods

2.5.1. Chemical and odor analysis

The compounds attracted by the SPME fiber were analyzed using a MDGC-MS-O (Microanalytics, Round Rock, TX) which integrates GC-O with conventional GC-MS (Model 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 two columns in series connected by a Dean's switch. The non-polar pre-column was 12 m, 0.53 mm i.d.; film thickness, 1 μm with 5% phenyl methylpolysiloxane stationary phase (SGE BP5) and operated with constant pressure mode at 8.5 psi. The polar analytical

column was a 30 m × 0.53 mm fused silica capillary column coated with poly(ethylene glycol) (WAX; SGE BP20) at a film thickness of 1 μm. The column pressure was constant at 5.8 psi. The use of two columns with opposite polarity results in improveved separation of a complex matrix such as VOCs emitted from swine barn. Separations on a non-polar column is mainly due to the molecular weights and boiling points of compounds, while separation on a polar column is due the difference in polarity and compound structure. System automation and data acquisition software were MultiTraxTM V. 6.00 and AromaTraxTM V. 6.61, from Microanalytics and ChemStationTM, from Agilent. The general run parameters used were as follows: injector temperature, 260 ºC; FID temperature, 280 ºC; column temperature, 40 ºC initial; 3 minutes hold, 7 ºC/minute, 220 ºC final, 10 minutes hold; carrier gas, He. Mass/molecular weight-to-charge ratio (m/z) range was set between 33 and 280. Spectra were collected at 6/s rate and electron multiplier voltage was set to 1500 V. The MS detector was auto-tuned weekly. More detail information related to the instrumentation has been described by Lo et al. (2007).

Compounds were identified with three sets of criteria: (1) matching 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 Bench-Top/PBM (from Palisade Mass Spectrometry, Ithaca, NY) and (3) matching odor character. Qualitative assessment of VOC abundance was measured as area counts under peaks for separated VOCs. Human

panelists were used to sniff separated compounds simultaneously with chemical analyses.

2.5.2. Statistical analysis

Analysis of variance (ANOVA) was used to test the main experimental factors of wood chip type (WC, HW), media moisture (20%, 40%, 60%), and EBRT (1.6, 2.5, 2.6, 3.3, 3.6, 4.0, 5.3, 5.5, and 7.3 seconds) using SAS (v. 9.1) for response variable percent reduction (reduction efficiency) of different principal odorous compounds. The reduction efficiency of each compound was transformed to natural logarithm to adjust for unequal variance and was tested using the main experimental factors listed above and its interactions. Tukey-Kramer adjustment for multiple comparisons was used.

3. Results and discussion

3.1. Selection of SPME fibers

Five new commercial SPME fiber coatings (85 µm Carboxen/PDMS, 65 µm PDMS/DVB, 50/30 µm DVB/Carboxen/PDMS, 85 µm PA and 100 µm PDMS; Supelco, Bellefonte, PA) were evaluated for determination of VOCs. Figure 4a shows the comparison of extraction efficiency between the five SPME fiber coatings for eleven characteristic swine odorants which included: acetic acid, propanoic acid, butanoic acid, isovaleric acid, pentanoic acid, hexanoic acid,

phenol, p-cresol, 4-ethyl phenol, indole, and skatole. All extractions were performed for 30 min using the SPME sampling system (Figure 3). No attempt was made to alter the gas temperature passing over the SPME fibers. The 65 μm PDMS/DVB and 85 μm Car/PDMS fibers were overall, the most effective for all target compounds among the five types of the fibers. Eight SPME samples were then collected again using both the 65 μm PDMS/DVB and 85 μm Car/PDMS fibers (four replicate samples for each fiber coating).

The comparison results between the 65 μm PDMS/DVB and 85 μm Car/PDMS fibers are shown in Figure 4b which indicates that for acetic acid, propanoic acid, and butanoic acid, the 85 μm Carboxen/PDMS fiber had higher extraction efficiency. However for p-cresol and skatole, the 65 μm PDMS/DVB fiber performed better. For the rest of the compounds; isovaleric acid, pentanoic acid, hexanoic acid, phenol, 4-ethyl phenol and indole, both fibers were equally effective. The compound p-cresol has been implicated as being the highest ranking odorant responsible for the characteristic odor near the source and far downwind (Bulliner et al., 2006; Koziel et al., 2006; Wright, et al., 2005). As a result of these findings, PDMS/DVB was selected for preferential extraction of p-cresol. Based on these results and previous experiences, the 65 μm PDMS/DVB fiber was selected for this study.

3.2. Effects of SPME sampling time on target odorants from swine barn

SPME sampling time was varied from 10 seconds to 2 hours to determine the optimal SPME extraction conditions by using 65 µm PDMS/DVB fibers. The plots of peak area of characteristic compounds versus extraction time are shown in Figures 5a and 5b which show that as extraction time increased so did the amount of most volatiles extracted by the fiber, however the patterns were not the same for all compounds. Most compounds, such as hexanoic acid, p-cresol, 4-ethyl phenol, indole and skatole, appeared to follow a linear trend, although at different adsorption rates, with no evidence of reaching equilibrium up to 2 hours extraction time. Butanoic acid and isovaleric acid showed an increasing trend with longer extraction time and then leveled after 30-60 minutes. However, the extraction amount of acetic acid and propanoic acid decreased with longer extraction time and then leveled. This trend was due to the porous structure of the 65 µm PDMS/DVB fiber which can easily become saturated when using prolonged extraction times (Jia et al. 2000; Woolfenden 1997). Once this occurs, compounds with higher affinity for the fiber will essentially displace those compounds with lower affinity. This can be minimized when shorter extraction times are used (Koziel et al. 2000; Zabiegala et al. 2000). The linearities (R^2) for times from 10 seconds up to 10 min for the 11 compounds are listed in table 1.

These R^2 values, except for acetic acid, illustrate nearly linear uptake of these target gases on SPME fibers during sampling. Linear uptake is an indication that no displacement effects were observed and that the peak area counts for each compound (and therefore also the measured concentrations) were not affected

by limited sorptive capacity of SPME fibers. Based on these results, an air sampling time of 10 minutes was chosen for all SPME extractions.

3.3. Mean peak area counts versus EBRT

There are several chemical compounds which are the main sources of offensive odors from swine buildings. Hammond et al. (1979) identified the organic acids, propanoic, butanoic, phenyl-acetic, and 3-phenyl-propanoic, as well as phenol, p-cresol, and 4-ethyl phenol, as important odor contributors. Wright et al. (2005) ranked p-cresol, indole, and skatole as the major odorants and assigned lower ranking to acetic acid and phenol. However, acetic acid and phenol are typically present at higher concentrations in these environments. Cai et al. (2006) also reported key malodorants associated with swine barn particulate matter including methyl mercaptan, isovaleric acid, p-cresol, indole and skatole In this study, SPME fibers were used to identify the odorous compounds exhausted from both the control plenum and biofilter treatments (WC, HW). The mean peak area counts of the odorous compounds detected in the control plenum and from the treatment reactors were used to compare the reduction efficiency between treatments as percent reduction, i.e., as the ratio of the difference between the control and treatment to the control, of the form (Cai et al, 2007):

$$\% Reduction = \frac{C_i - T_i}{C_i} \times 100\% \qquad (1)$$

Where:

C_i = peak area count of compound "i" for the control, and

T_i = peak area count of compound "i" for the treatment.

The percentage reduction of specific compounds reported in this paper is based on qualitative evaluations and use of 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 based on estimates of concentrations (Cai et al., 2007). 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 [1] is used for qualitative comparisons. More research is warranted to test these assumptions with alternative air sampling and analysis methods.

The same approach was used by Cai et al (2007) to determine the reduction of odorous gases from treated and untreated poultry manure. Cai et al (2007) used a 10 minute air sampling time with SPME from manure headspace followed by analyses on GC-MS-O and used the area count percent reduction as given in equation (1) which is consistent with an assessment of concentration reduction.

The mean peak area counts were calculated using the integrated area of a single ion. The results with standard errors (n=3) are shown in Figures 6a, b, c, d.

The higher reduction of WC for acetic acid, phenol, p-cresol and skatole compared to HW (Figures 6a, b, c, d) could be due to the higher porosity of the WC compared to HW. It is also important to mention that indole was not detected from either the WC or HW treatments using the GC-MS, although the odor associated with indole were detected at the olfactory port by the panelists from the HW treatment at the 5.3 s EBRT. This indicates that the concentration of indole was below the detection capability of the GC-MS but still above the recognition threshold for the panelists.

Odorous gases emitted from swine manure are very complex mixtures from hundreds of odorous compounds (Lo et al., 2008; O'Neill and Phillips, 1992; Schiffman et al., 2001). However, it is generally agreed that only some chemical groups of compounds are likely contributors of the odor nuisance (Nettenbreijer, 1977; O'Neill and Phillips, 1992; Van Gemert and Schaefer, 1977; Yasuhara, et al., 1984). Generally there are four chemical groups reported by the above researchers: VFAs, sulfur containing compounds, phenolics and indolics. A summary of the reduction efficiency, estimated with equation (1), for the four groups of characteristic compounds is given in Tables 2a, b.

The compound removal efficiencies, based on overall average, were very good for both types of biofilter media ranging from 76% to 92.6% (Tables 2a, b). Particularly noteworthy is the removal of p-cresol which has been cited as the major odorant responsible for downwind swine odor (Koziel et al., 2006). The reduction of p-cresol, averaged over all EBRTs, was 99.9% and 95.3 % for WC and HW, respectively. The reduction efficiencies shown in Tables 2a and 2b

have no discernable trend relative to EBRT. The most likely reason for this was that the media was maintained at a high moisture content of 60%. These results indicate that for biofilter design and operation, a higher media moisture content is most important. The relationship between moisture content, EBRT and reduction efficiencies for the characteristic compounds need to be further investigated.

The WC treatment achieved maximum removal efficiencies for VFAs up to 99.8% with a minimum efficiency of 96.1%. The HW treatment achieved maximum removal efficiencies for VFAs up to 99.7% with a minimum efficiency of 86.8%. This high peak area reduction efficiency was most likely the result of the VFAs having a low volatility (Henry's law constant) and a high water solubility making them easily dissolved in the surface water of the high moisture content media.

The WC treatment achieved a maximum removal efficiency of 74.9% and a minimum removal of 16.9% for sulfur-containing compounds while the HW treatment achieved a maximum efficiency of 67.9% and a minimum removal of 12.8%. Sheridan et al. (2002) reported sulfur-containing compounds were reduced between 8-65% and -147-50% across two biofiltration systems made from two different sizes of wood ships. The relatively low reduction efficiency for the sulfur-containing compounds (compared to VFA, phenolic and indolic groups) was most likely the result of anaerobic zones (excess interstitial water) within the biofilter bed where organisms can create sulfur-containing organics (Devinny et al, 1999; Sheridan et al. 2002).

For the phenolic compounds, the reduction efficiencies for WC were between 98.6% and 94.6% and the reduction efficiencies for HW were between 98.1% and 85.5%. For the indolic compounds, the reduction efficiencies were above 98.3% for WC and above 97.5% for HC, respectively.

The ANOVA analysis results of reduction efficiencies for the 11 target compounds are shown in Table 3 which indicates that there were significant differences between the two media treatments among the 9 EBRT levels except for hexanoic acid, indole and isovaleric acid. These three compounds were below the GC-MS detection limit for both the WC and HW treatments indicating that the removal efficiency was nevertheless very high.

3.4 Reduction efficiency comparison versus media moisture

Moisture is needed to maintain microbial activity during biofiltration processes. Several studies have reported that biofilter media moisture is one of the key factors when biofilters are used for treating odors (Hartung et al., 2001; Nicolai et al., 2006; Sun et al., 2000). Moisture levels between 40%-60% (wet basis) have been suggested for biofilter operation (Kastner, 2004; Nicolai and Janni, 2001b). In this study, SPME samples were collected and analyzed at three levels of media moisture content (60%, 40% and 20% wet basis) with a fixed media depth of 25 cm and a fixed air flow rate of 2, 265 L/minute (EBRT = 1.6 s). Figures 7a, b, c, d, e show the results attained in this study.

Increasing both the WC and HW media moisture improved the reduction efficiencies for the five main compounds as shown in Figures 7a, b, c, d, e, respectively. This could be the result of a higher moisture level absorbing these compounds along with the maintenance of a better environment for bacteria growth. Several studies conducted on odor, H_2S and NH_3 reductions obtained similar trends as those found in this study. Sun et al. (2000) reported that a higher media moisture content resulted in a higher removal efficiency for H_2S (47%-94%) and NH_3 (25%-90%) corresponding to moisture contents of 30-50%, respectively, when the compost-based biofilter was used to treat odorous gas. Nicolai et al. (2006) observed that increasing the moisture content from 40% to 50% (wet basis) increased removal efficiency of NH_3 from an average of 76.7% to 82.3% and increasing the moisture content to 60% did not significantly change the removal efficiency with a compost/wood chip biofilter. These results confirmed that the media moisture plays a key role in the biofiltration processes.

The results shown in Figures 7a, b, c, d, e also indicate that WC performed better than HW at all moisture levels except the reduction efficiency for p-cresol and phenol at the 20% moisture level. The reduction efficiencies of WC for moisture levels between 20-60% were between 32%-77% for acetic acid, 19%-96% for phenol, above 49% for p-cresol, above 73% for indole and above 53% for skatole. The reduction efficiencies of HW for moisture levels between 20-60% were between 14%-77% for acetic acid, 55%-93% for phenol, 72%-98% for p-cresol, above 75% for indole and 52%-96% for skatole. A summary of the reduction efficiencies at three levels of media moisture content, estimated with

equation (1), for different compounds arranged by the four groups of characteristic compounds is given in Tables 4a, b. The reduction efficiencies for VFAs, phenolics, indolics and the overall average for all compounds increased with higher media moisture level. There was no significant improvement when the moisture level was raised from 40% to 60% for WC but there was significant improvement for HW over this same range. For the sulfur-containing compounds, the reduction efficiency decreased when the media moisture level increased above 20% for both WC and HW. The most likely reason was the development of anaerobic zones as proposed by Devinny et al. (1999).

The WC biofilter can achieve relatively high removal efficiencies (93.8%, 97.2%, 97.8%, and 74% for VFAs, phenolics, indolics and overall average for all compounds, respectively) at a lower moisture content (40%) while the HW biofilter needed a higher moisture content (60%) to achieve the same reduction efficiencies for these compounds (Tables 4a, b). For the sulfur-containing compounds, HW performed better than WC at all levels of media moisture.

4. Conclusions

A pilot-scale mobile biofilter was developed where WC and HW chips were examined to treat odor emissions from a deep-pit swine finishing facility in central Iowa. The fate of characteristic odorous compounds was investigated. The results of this study demonstrated that both the WC and HW chips achieved high overall average reduction efficiency (at least 76% and as high as 93%) for

20

treating characteristic compounds when the biofilter media moisture content was kept at 60% (wet basis). The reduction efficiency testing at three media moisture levels indicated that the biofilter, whether WC or HW, was more sensitive to the media moisture content than media depth or EBRT. Therefore, maintaining proper moisture content is critical to the proper operation of wood chip-based biofilters. Moisture content is more important than media depth and EBRT when a wood chip-based biofilter is operated. The high reduction efficiency obtained with the wood chip-based biofilter media studied in this research suggests that these materials can be used effectively as biofilter media for reducing swine building odors.. However, more studies at full scale biofilters are needed.

Acknowledgements

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Figure Captions

Fig. 1a. Mobile pilot-scale biofilter laboratory and monitoring laboratory.

Fig. 1b. Plan view layout of the biofilter testing laboratory.

Fig. 2a. Eight total reactor barrels inside the biofilter testing laboratory.

Fig. 2b. SPME sampling port with SPME fibers.

Fig. 2c. Hardwood (HW) and western cedar (WC) media.

Fig. 3. Schematic of the gas and SPME sampling systems.

Fig. 4a. Comparison of extraction efficiency between five SPME fiber coatings tested.

Fig. 4b. Comparison of extraction efficiency between the 65 µm PDMS/DVB fibers and the 85 µm Car/PDMS fiber coatings for eleven characteristic swine odorants. Extraction time= 30 min.

Fig. 5a. Plot of peak area counts for the characteristic VFA compounds versus extraction time by using 65 µm PDMS/DVB fiber.

Fig. 5b. Plot of peak area counts for the characteristic phenolic and indolics compounds versus extraction time by using 65 µm PDMS/DVB fibers.

Fig. 6a. Comparison of peak area count as a function of EBRT for acetic acid.

Fig. 6b. Comparison of peak area count as a function of EBRT for phenol.

Fig. 6c. Comparison of peak area count as a function of EBRT for p-cresol.

Fig. 6d. Comparison of peak area count as a function of EBRT for skatole.

Fig. 7a. Comparison of area counts as a function of media material and moisture content for acetic acid.

Fig. 7b. Comparison of area counts as a function of media material and moisture content for phenol.

Fig. 7c. Comparison of area counts as a function of media material and moisture content for p-cresol.

Fig. 7d. Comparison of area counts as a function of media material and moisture content for indole.

Fig. 7e. Comparison of area counts as a function of media material and moisture content for skatole.

Table 1

Summary of the coefficients of determination (R^2) for SPME extraction times from 10 sec up to 10 min for the 11 target compounds

Compounds	R-square
Acetic acid	0.0221
Propanoic acid	0.7677
Butanoic acid	0.9713
Isovaleric acid	0.9919
Pentanoic acid	0.9982
Hexanoic acid	0.9502
Phenol	0.8837
p-Cresol	0.9978
4-Ethyl phenol	0.9938
Indole	0.9976
Skatole	0.9976

Table 2a

Reduction efficiencies of characteristic compounds based on equation (1) for western cedar at moisture level of 60%

Compounds \ EBRT (s)	1.6	2.5	2.6	3.3	3.6	4	5.3	5.5	7.3	Average over EBRT (%)
VFAs										
Acetic acid (%)	76.7	95.2	92.5	100.0*	92.8	90.6	98.6	97.6	76.3	91.1
Propanoic acid (%)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Butanoic acid (%)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.8	100.0	100.0
Isovaleric acid (%)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Pentanoic acid (%)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Hexanoic acid (%)	100.0	100.0	100.0	**	100.0	100.0	100.0	100.0	100.0	100.0
Average for VFAs	96.1	99.2	98.8	100.0	98.8	98.4	99.8	99.6	96.1	98.5
Sulfide compounds										
Methyl mercaptan (%)	-44.2	17.2	29.0	32.6	63.5	48.3	-91.8	52.3	43.1	16.7
Dimethyl sulfide (%)	100.0	**	**	**	100.0	**	100.0	**	**	100.0
Dimethyl disulfide (%)	**	**	**	**	100.0	**	**	100.0	80.6	93.5
3-Methyl thiophene (%)	39.0	49.8	76.7	46.4	36.5	1.3	52.9	63.5	**	45.8
Dimethyl trisulfide (%)	-27.3	37.0	86.5	14.0	58.2	47.5	21.0	83.9	**	40.1
Average for sulfide compounds	16.9	34.7	64.1	31.0	71.6	32.4	20.5	74.9	61.8	59.2
Phenolics										
Phenol (%)	95.6	95.5	95.2	95.8	95.1	93.2	95.9	92.3	83.9	93.6
p-Cresol (%)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	98.9	100.0	99.9
4-Ethyl phenol (%)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Average for phenolics	98.5	98.5	98.4	98.6	98.4	97.7	98.6	97.1	94.6	97.8
Indolics										
Indole (%)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Skatole (%)	100.0	100.0	100.0	96.7	100.0	100.0	100.0	100.0	100.0	99.6
Average for indolics	100.0	100.0	100.0	98.3	100.0	100.0	100.0	100.0	100.0	99.8
Overall average	76.0	85.3	91.4	82.1	90.4	84.3	78.4	92.6	91.1	86.3

* 100% removal efficiency signifies that a compound was not detected in treated exhaust

∗* This compound was below detection limits in both the control plenum and treated exhaust.

Table 2b

Reduction efficiencies of characteristic compounds based on equation (1) for hardwood chips at moisture level of 60%

Compounds \ EBRT (s)	1.6	2.5	2.6	3.3	3.6	4	5.3	5.5	7.3	Average over EBRT (%)
VFAs										
Acetic acid (%)	76.8	88.2	87.5	100.0*	88.6	80.0	98.4	96.1	34.8	83.4
Propanoic acid (%)	100.0	100.0	100.0	100.0	94.9	100.0	100.0	98.2	100.0	99.2
Butanoic acid (%)	100.0	99.2	99.0	100.0	94.8	98.0	99.8	99.0	86.2	97.3
Isovaleric acid (%)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Pentanoic acid (%)	100.0	100.0	100.0	100.0	95.4	100.0	100.0	99.3	100.0	99.4
Hexanoic acid (%)	100.0	100.0	100.0	**	100.0	100.0	100.0	100.0	100.0	100.0
Average for VFAs	96.1	97.9	97.8	100.0	95.6	96.3	99.7	98.8	86.8	96.6
Sulfide compounds										
Methyl mercaptan (%)	30.9	1.2	27.1	33.4	5.8	-44.1	-30.5	35.8	6.7	7.4
Dimethyl sulfide (%)	100.0	**	**	28.6	19.0	**	100.0	**	100.0	69.5
Dimethyl disulfide (%)	**	**	**	22.7	100.0	**	**	100.0	64.8	71.9
3-Methyl thiophene (%)	39.4	27.9	39.4	69.6	43.1	34.6	-3.7	45.2	100.0	43.9
Dimethyl trisulfide (%)	-38.8	40.4	30.7	32.0	64.5	47.9	11.2	46.1	**	29.3
Average for sulfide compounds	32.9	23.2	32.4	37.3	46.5	12.8	19.2	56.8	67.9	44.4
Phenolics										
Phenol (%)	92.8	94.4	93.5	94.2	90.4	93.8	94.9	89.3	75.5	91.0
p-Cresol (%)	97.7	99.3	97.7	100.0	90.3	98.8	98.8	93.9	81.1	95.3
4-Ethyl phenol (%)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	93.2	100.0	99.2
Average for phenolics	96.8	97.9	97.1	98.1	93.6	97.5	97.9	92.1	85.5	95.2
Indolics										
Indole (%)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Skatole (%)	95.6	100.0	100.0	95.6	100.0	96.6	94.9	100.0	100.0	98.1
Average for indolics	97.8	100.0	100.0	97.8	100.0	98.3	97.5	100.0	100.0	99.0
overall average	79.6	82.2	83.9	76.9	80.4	79.0	77.6	86.4	83.3	80.3

* 100% reduction efficiency signifies that a compound was not detected in treated exhaust

** This compound was not detected in both the control plenum and treated exhaust.

Table 3

P-values of ANOVA analysis of reduction efficiencies for 8 characteristic

compounds

Factors	4-Ethyl phenol	Acetic acid	Butanoic acid	Pentanoic acid	Phenol	Propanoic acid	Skatole	p-Cresol
Media	<.0001	0.027	<.0001	<.0001	0.0003	<.0001	<.0001	<.0001
EBRT	<.0001	0.0007	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001
Media*EBRT	<.0001	0.019	<.0001	<.0001	0.054	<.0001	<.0001	<.0001

Table 4a

Reduction efficiencies at 1.6 sec EBRT for western cedar

Compounds \ Moisture content (%)	20	40	60	average over all moisture content (%)
VFAs				
Acetic acid (%)	32.2	62.6	76.7	57.1
Propanoic acid (%)	-6.5	100.0*	100.0	64.5
Butanoic acid (%)	2.4	100.0	100.0	67.5
Isovaleric acid (%)	14.5	100.0	100.0	71.5
Pentanoic acid (%)	3.5	100.0	100.0	67.8
Hexanoic acid (%)	100.0	100.0	100.0	100.0
average for VFAs	24.3	92.5	96.1	71.0
Sulfide compounds				
Methyl mercaptan (%)	5.6	1.7	-44.2	-12.3
Dimethyl sulfide (%)	56.2	100.0	100.0	85.4
Dimethyl disulfide (%)	100.0	50.8	**	75.4
3-Methyl thiophene (%)	31.2	-27.4	39.0	14.3
Dimethyl trisulfide (%)	23.9	35.2	-27.3	10.6
average for sulfide compounds	43.4	32.1	16.9	30.8
Phenolics				
Phenol (%)	18.8	92.7	95.6	69.0
p-Cresol (%)	48.7	99.0	100.0	82.6
4-Ethyl phenol (%)	58.1	100.0	100.0	86.0
average for phenolics	41.9	97.2	98.5	79.2
Indolics				
Indole (%)	73.3	100.0	100.0	91.1
Skatole (%)	52.5	95.5	100.0	82.7
average for indolics	62.9	97.8	100.0	86.9
overall average	38.4	74.0	76.0	62.8

* 100% reduction efficiency signifies that a compound was not detected in treated exhaust

* *This compound was not detected in both the control plenum and treated exhaust.

Table 4b

Reduction efficiencies at 1.6 sec EBRT for hardwood chips

Compounds \ Moisture content (%)	20	40	60	average over all moisture content (%)
VFAs				
Acetic acid (%)	13.8	31.6	76.8	40.8
Propanoic acid (%)	35.7	66.9	100.0*	67.5
Butanoic acid (%)	45.2	72.0	100.0	72.4
Isovaleric acid (%)	47.4	100.0	100.0	82.5
Pentanoic acid (%)	55.3	100.0	100.0	85.1
Hexanoic acid (%)	100.0	100.0	100.0	100.0
average for VFAs	49.6	78.4	96.1	74.7
Sulfide compounds				
Methyl mercaptan (%)	36.9	29.0	30.9	32.3
Dimethyl sulfide (%)	41.6	37.3	100.0	59.6
Dimethyl disulfide (%)	100.0	58.9	**	79.4
3-Methyl thiophene (%)	11.8	9.9	39.4	20.4
Dimethyl trisulfide (%)	59.5	16.6	-38.8	12.4
average for sulfide compounds	50.0	30.3	32.9	37.7
Phenolics				
Phenol (%)	54.7	58.2	92.8	68.5
p-Cresol (%)	72.3	70.8	97.7	80.3
4-Ethyl phenol (%)	68.6	67.2	100.0	78.6
average for phenolics	65.2	65.4	96.8	75.8
Indolics				
Indole (%)	75.4	75.3	100.0	83.6
Skatole (%)	51.6	57.1	95.6	68.1
average for indolics	63.5	66.2	97.8	75.8
overall average	54.4	59.4	79.6	64.5

* 100% removal efficiency signifies that this compound was not detected in treated exhaust

** This compound was not detected in both the control plenum and treated exhaust.