Testing the effectiveness of a naturally occurring adsorbent to improve mitigation of multiple air emissions from swine buildings – NPB #13-026

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Industry Summary:

Objectives: Biofiltration is a proven method to reduce odor and gas emissions from swine buildings and manure storage units. Biofilter media selection and moisture content fluctuations significantly influence biofilter performance. Media with significant amounts of small particles have higher static pressure drops which lowers airflow through the biofilter. Inadequate moisture can reduce biological activity and decrease filter effectiveness. Too much moisture (following a watering or rainfall event) can plug media pores, restrict airflow through the media, produce anaerobic pockets and generate nitrous oxide (N₂O). In this study, a naturally occurring adsorbent (diatomaceous shale) was used as an additive to manage biofilter media moisture content. Also, corn cobs were tested as an alternative biofilter media because wood chips are expected to be less available in near future due to emerging emerald ash borer disease. The objectives of the study were to 1) Measure water adsorption and desorption capacities of the diatomaceous shale, 2) Test the effectiveness of the corn cobs as biofilter media and diatomaceous shale as a biofilter media additive, and 3) Estimate the cost of using the diatomaceous shale as a biofilter media additive.

How research was conducted: The experiments were conducted at the University of Minnesota West Central Research and Outreach Center (WCROC, Morris, MN). Five 3.3 ft × 3.3 ft × 3.3 ft wooden biofilter cells were built to treat air from pit fans on a swine finishing barn. Four cells were filled with whole corn cobs. One of the four cells contained no diatomaceous shale and the other three cells contained 5, 10, or 15% (by volume) shale. The fifth cell was filled with wood chips. The media depths were- wood chips: 0.5 m, corn cobs: 3.3 ft, corn cobs with 5, 10, and 15% shale: 3 ft. Each cell had its own air blower that pulled air from a duct connected to two exhaust pit fans.

Media characteristics (water absorption capacity, porosity, density and pressure drops across the media) were measured as described in previous studies. A semi-continuous sampling system was used to measure biofilter cells’ inlet and outlet gas concentrations. Gas sampling started on September 12, 2013 and continued until November 22, 2013. The GSS sampled six sample lines and the ambient airline for 15 min 14 times a day and daily averages were calculated using 14 sample averages.

Discussion of the findings: Diatomaceous shale was found to have good water adsorption capacity but superior desorption capacity (desorbs most of the water it adsorbs when relative humidity of the environment is 50%) unlike other adsorbents (e.g., activated carbon, diatomaceous earth, zeolite) that can desorb less than 5% of the water they adsorb in 24 hours.
The corn cobs were less dense and more porous than the wood chips at all moisture levels tested. At wet conditions (60 and 74% moisture levels), wood chips had low porosity, which may result in anaerobic pocket formation and nitrous oxide generation. At any moisture level and mixing ratio corn cobs’ porosity values were above 25%. The cobs had more than 100% moisture absorption capacity at dry conditions (13.5%) while the absorption capacity of the wood chips was 57%.

Wood chips had the lowest percent gas reduction efficiencies; ability to remove gases from manure pit ventilation air. Corn cobs with 15% shale had the highest percent reduction efficiencies, followed by corn cobs with 10% shale and corn cobs with 5% shale. The average H$_2$S and NH$_3$ percent reduction efficiencies of corn cobs with 15% shale were much higher than those of corn cobs without shale (cobs with 15% shale- H$_2$S: 86%, NH$_3$: 50%; cobs without shale-H$_2$S: 13%, NH$_3$: 12%). The high percent reduction efficiency of the cobs with shale was probably due to shale’s good moisture adsorption and desorption capacity. Inlet and outlet N$_2$O concentrations of the biofilter cells were close to each other and no N$_2$O generation was observed even after water was added. The estimated cost of the corn cob media with 15% diatomaceous shale was $0.88 per cubic feet per minute (cfm) air treated. The corn cobs cost was less than $0.05 per cfm air treated.

**What these findings mean to the industry:** Corn cobs with 15% diatomaceous shale can be used as biofilter media to treat H$_2$S and NH$_3$ emissions from swine buildings. Corn cobs are another biofilter media option if wood chips become unavailable due to emerging emerald ash borer disease. Corn cobs would be a good alternative media with excellent moisture absorption capacity. Although using diatomaceous shale increases cost, it significantly improves gas reduction efficiencies and reduces the need for a watering system. Useful life of corn cobs as biofilter media still needs to be determined.

**Introduction:**
Biofiltration is a proven method to reduce odor and gas emissions from swine buildings and manure storage units. Biofilters are used to treat air from mechanically ventilated buildings, pit fans, and covered manure storage facilities. Biofilters can be used to treat 100% of the exhaust air or they can be used to treat a
critical minimum amount of ventilation air during the evening and morning hours when atmospheric conditions are stable (Hoff et al., 2009). They are also used to treat air from pit fans on naturally ventilated barns (Janni et al., 2011a). Although biofilters are shown to reduce odor and hydrogen sulfide (H₂S) emissions by up to 95% and ammonia (NH₃) emissions by 80% (Janni et al., 2011a), fluctuations in media moisture content significantly influence biofilter gas removal performance. Lack of media moisture control was reported to cause up to 75% of all biofiltration problems (Nicolai and Lefers, 2006). Inadequate moisture can reduce filter efficiency by creating cracks that allow air channeling and by decreasing biological activity (Janni et al., 2011a). Biofilters with higher moisture contents were shown to have the best removal for both H₂S and NH₃ (Sun et al., 2000; Akdeniz and Janni, 2012). However, too much moisture can plug media pores, cause channeling, restrict airflow through the media, and limit oxygen flow in saturated media areas. Saturated areas can form anaerobic pockets within the media and generate anaerobic gases such as nitrous oxide (Clemens and Chuls, 2003; Del Nero Maia et al., 2008; Janni et al., 2011a; Akdeniz and Janni, 2012). Nitrous oxide (N₂O) is an important greenhouse gas, which is produced when aerobic media becomes anaerobic. Initially under aerobic conditions nitrogen oxides (NOₓ) are produced and after becoming anaerobic the NOₓ are converted to nitrogen (N₂) with intermediate production of N₂O. This commonly happens when dry biofilter media gets wet in heavy rain (Akdeniz and Janni, 2012). Janni et al. (2011b) reported that for a 3.5 years old wood chips flat-bed biofilter the inlet (exhaust air from a nursery barn) N₂O concentrations were around 400 ppb while the biofilter outlet N₂O concentrations could reach up to 2,200 ppb.

The importance of biofilter media moisture control has led to research to develop and assess sensors to monitor moisture levels in biofilters (Robert et al., 2005; Yang et al., 2012; Yang et al., 2013). Although impedance based moisture sensors were developed, they were not found to be sensitive at different temperatures (Yang et al., 2013). Currently, there are no commercially available biofilter moisture sensors.

Akdeniz and Janni (2012) reported that a flat-bed biofilter with fine-particle wood chips can generate N₂O, increasing inlet N₂O concentrations that ranged from 403 to 666 ppb by up to 29%. Biofilters with large wood chips and shredded wood generate little N₂O and have lower pressure drops across the media (Akdeniz and Janni, 2012). To prevent N₂O generation and lower the fan energy required pushing air through the filter; it was suggested to use larger size media. However, a concern with using large wood chips or shredded wood as biofilter media is that the wood may carry emerald ash bore (EAB) larvae. EAB is an invasive insect which has killed tens of millions of ash trees since 2002. McCullough et al. (2003) reported that wood chips should be ground to a one-inch size to adequately destroy all EAB larvae and larger chips should not be stored, they should be incinerated promptly. Minnesota is especially vulnerable to EAB attacks since it has more ash trees than other states. Ash trees are a component of windbreaks, shelterbelts, and lowlands (Hoff, 2009). Regulatory agencies and the U.S. Department of Agriculture (USDA) have enforced quarantines and fines in Minnesota and 14 other states (Illinois, Indiana, Iowa, Kentucky, Maryland, Michigan, Missouri, New York, Ohio, Pennsylvania, Tennessee, Virginia, West Virginia, and Wisconsin) to prevent the spread of EAB (APHIS, USDA, 2014). Although, EAB only affects ash trees, the Department of Agriculture has quarantined all hardwood chips and barks since once a log has been cut and split, it is extremely difficult to differentiate between ash wood and other hardwood species.

In this study, the gas removal efficiency of an alternative biofilter media, corn cobs, and a naturally occurring adsorbent, diatomaceous shale, were tested. Corn cobs are widely available in Minnesota from July to October and have good water absorption capacity and porosity (Fuchs, 2007). Diatomaceous shale is a type of diatomaceous earth and has been used to control indoor air humidity (Katsunori et al., 2008). This shale is more efficient for controlling humidity than other naturally occurring adsorbents since it has a mesoporous structure. Naturally occurring adsorbents (i.e., diatomaceous earth, zeolite) are generally amorphous (having no apparent shape or organization) and contain complex networks of inter-connected micropores (<20 Å), mesopores (20 to 500 Å) and macropores (>500 Å). Diatomaceous shale is naturally heat treated and mainly contains mesopores (20-60 Å). Mesopores are mainly responsible for capillary condensation which is often accompanied by hysteresis. Hysteresis can be defined as the dependence of a system not only on its current environment but also on its past environment. During adsorption, when a capillary’s radius increases sharply, adsorption ceases until an equilibrium vapor pressure is reached, which satisfies the larger pore size. However, during desorption,
liquid remains filled in the larger pores until an equilibrium vapor pressure that satisfies the smaller pore size is reached (Lakatos, 2011). Therefore, mesoporous adsorbents have good water adsorption and superior water desorption capacities.

**Objectives:**

**Objective 1:** To measure water adsorption and desorption capacities of the diatomaceous shale

**Objective 2:** To test the effectiveness of the corn cobs as biofilter media and diatomaceous shale as a biofilter media additive

**Objective 3:** To estimate the cost of using the diatomaceous shale as a biofilter media additive

**Materials & Methods:**

**Diatomaceous shale’s water adsorption and desorption capacity**

Water adsorption and desorption capacities of the diatomaceous shale were measured at 90% and 50% relative humidity, respectively. Measurements were done in an environmental chamber held at 20°C. One hundred grams of oven dried diatomaceous shale were placed inside an Erlenmeyer flask with air inlet and outlet ports. First, air at 90% relative humidity was pumped inside the flask (40 mL/min) using a low-flow vacuum pump (SKC 210-1002MH, Eighty Four, PA). Relative humidity of the air was adjusted by using a glass impinger (SKC Inc., Eighty Four, PA) and measured with a digital relative humidity sensor (HM70, Vaisala, Louisville, CO). Twenty-four hours later weight difference was measured (±0.001) and water adsorption capacity (%) of the diatomaceous shale was calculated. Then, air at 50% relative humidity was pumped inside the flask for 24 hours and water desorption capacity of the adsorbent was measured. Experiments were run in triplicate.

**Sampling site**

The experiments were conducted at the University of Minnesota West Central Research and Outreach Center (WCROC, Morris, MN). Five 1 m × 1 m × 1 m wooden biofilter cells were built to treat air from pit fans on a swine finishing barn (Figure 1). Four cells were filled with whole corn cobs. One of the four cells contained no diatomaceous shale and the other three cells contained 5, 10, or 15% (by volume) shale. The fifth cell was filled with wood chips. No amendments were added to the wood chips. Corn cobs were provided by the WCROC and wood chips were purchased from a local store. Treatments were assigned to the cells randomly. The initial media depth of each cell was adjusted such that all cells had the same pressure drop (18.7 Pa) at the beginning of the experiment. The media and adjusted depths were- wood chips: 0.5 m, corn cobs: 1 m, corn cobs with 5, 10, and 15% shale: 0.9 m. Wooden pallets were placed at the bottom of the cells to support media. Each cell had its own air blower (Dayton 6FHX5 forward curve direct drive) and the blowers pulled air from the air plenum that connected two pit fan exhausts. Each blower was rated for 3850 lpm at 25 Pa and 3550 lpm at 60 Pa. Preliminary experiments were run to make sure that the pit fan exhaust air was well mixed before air was blown into the biofilter cells by the blowers.
Figure 1. Pictures of the biofilter cells: a) five biofilter cells, b) corn cobs filled in a 1 m×1 m ×1 m cell, c) sampling lines that were connected to the sampling trailer, d) each cell’s individual air blower, e) wooden pellets, f) north pit fan exhaust and air plenum.

Media characteristics

Water absorption capacity, porosity, and density of the media (wood chips, corn cobs, corn cobs with 5% shale, corn cobs with 10% shale and corn cobs with 15% shale) were measured as described by Janni et al. (2009), Akdeniz et al. (2011), and Akdeniz and Janni (2012) at dry (13.5%), 35, 50, 60 and 74% (maximum water that could be held by the media without having any dripping) moisture levels.

Pressure drops across the media were measured at 40, 60, 80, 100 cm media depths and 13.5 and 74% moisture levels (Janni et al., 2009, Akdeniz et al., 2011, and Akdeniz and Janni, 2012).

In addition, during site visits, pressure drops across the media were measured with a manometer (Dwyer Instruments, Michigan City, IN). Also, media samples were collected from representative sampling locations (five or six locations) and media moisture contents were measured by weighing the media before and after oven drying at 105°C for 24 h. Wet basis media moisture contents were calculated by dividing weight of water to total weight of sample.

Gas measurements

A semi-continuous sampling system which was used in a number of projects including the National Air Emissions Monitoring Study (NAEMS) was used to measure biofilter cells’ inlet and outlet gas concentrations (Heber et al., 2008; Janni et al., 2013). The semi-continuous system sequentially drew sample air from six sampling locations: pit fan exhausts (inlet of the cells) and outlets of the cells (five cells). The air samples were delivered to the analyzers via a gas sampling system (GSS), which has PTFE tube sample lines connected to a computer controlled manifold. H₂S, NH₃, and N₂O concentrations were measured with a TEC 450i (Thermo Electron Corporation, Franklin, MA), TEC17C, and Teledyne 320EU (San Diego, CA), respectively. Analyzers were calibrated using certified calibration gases every week. Calibration cylinders were purchased from Toll Gas and Welding Company (Bloomington, MN).

Gas sampling started on September 12, 2013 and continued until November 22, 2013. The GSS sampled six sample lines and the ambient airline for 15 min 14 times a day and daily averages were calculated using 14 sample averages. While daily averages were calculated the last 10 min of data was used (first 5 measurements were not taken into account since instruments were allowed to stabilize during this time). A macro created in Microsoft Excel was used to calculate daily averages.

No water (other than rain water) was added from September 12, 2013 to November 11, 2013 and little rain water fell during that time (42 mm in September, 98 mm in October and 0 mm in November). Before November 11, the media moisture contents of the corn cobs, wood chips, 5 and 10% shale added cobs were around 12.5%. Only the moisture content of the cobs mixed with 15% shale was higher (55%). After November 11, water was added to the cells until a very little water started to leach from the bottom of the cells.
Results:

**Objective 1: To measure water adsorption and desorption capacities of the diatomaceous shale**

The water adsorption and desorption capacities of diatomaceous shale are shown in Fig 2. The shale adsorbed water up to 20% of its dry weight at 90% relative humidity and desorbed most of the water it adsorbed when the relative humidity was lowered to 50%. These results show that the shale has good adsorption capacity and superior desorption capacity unlike other adsorbents (e.g., activated carbon, diatomaceous earth, zeolite) that can desorb less than 5% of the water they adsorb in 24 hours (Natur Japan).

![Figure 2. Water adsorption and desorption capacities of the diatomaceous shale](image)

**Objective 2: To test the effectiveness of the corn cobs as biofilter media and diatomaceous shale as a biofilter media additive**

**Media characteristics**

Media density, porosity, and water absorption capacity are shown in Tables 1, 2, and 3, respectively. The corn cobs were less dense and more porous than the wood chips at all moisture levels. At 60 and 74% moisture levels, porosity values of the wood chips were low (9.5 and 0.8%, respectively), which may result in anaerobic pocket formation and nitrous oxide generation. At any moisture levels and mixing ratios corn cobs’ porosity values were above 25%. The cobs had more than 100% moisture absorption capacity at dry conditions (13.5%) while the absorption capacity of the wood chips was 57%.

<table>
<thead>
<tr>
<th>Table 1. Media density (kg/m³)</th>
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<tbody>
<tr>
<td>Media</td>
</tr>
<tr>
<td>Wood chips</td>
</tr>
<tr>
<td>Corn cobs</td>
</tr>
<tr>
<td>Corn cobs with 5% shale</td>
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<tr>
<td>Corn cobs with 10% shale</td>
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<td>Corn cobs with 15% shale</td>
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<table>
<thead>
<tr>
<th>Table 2. Media porosity (%)</th>
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<tbody>
<tr>
<td>Media</td>
</tr>
<tr>
<td>Wood chips</td>
</tr>
<tr>
<td>Corn cobs</td>
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<tr>
<td>Corn cobs with 5% shale</td>
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<tr>
<td>Corn cobs with 10% shale</td>
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<tr>
<td>Corn cobs with 15% shale</td>
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Table 3: Media water absorption capacity (%)

<table>
<thead>
<tr>
<th>Media</th>
<th>13.5%</th>
<th>35%</th>
<th>50%</th>
<th>60%</th>
<th>74%</th>
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</thead>
<tbody>
<tr>
<td>Wood chips</td>
<td>56.7±3.7</td>
<td>32.1±2.6</td>
<td>17.8±2.3</td>
<td>9.2±1.4</td>
<td>0.8±0.3</td>
</tr>
<tr>
<td>Corn cobs</td>
<td>125.4±4.8</td>
<td>90.2±4.6</td>
<td>63.6±2.4</td>
<td>31.2±4.0</td>
<td>11.1±1.5</td>
</tr>
<tr>
<td>Corn cobs with 5% shale</td>
<td>135.5±4.7</td>
<td>115.8±5.6</td>
<td>81.9±5.6</td>
<td>37.7±4.5</td>
<td>16.3±1.6</td>
</tr>
<tr>
<td>Corn cobs with 10% shale</td>
<td>145.0±4.4</td>
<td>130.9±5.6</td>
<td>89.9±3.9</td>
<td>42.7±7.8</td>
<td>21.5±1.5</td>
</tr>
<tr>
<td>Corn cobs with 15% shale</td>
<td>160.7±4.7</td>
<td>148.7±2.5</td>
<td>94.3±2.1</td>
<td>49.7±2.8</td>
<td>27.9±1.9</td>
</tr>
</tbody>
</table>

Pressure drops at 13 and 75% moisture levels are shown in Figure 3 and 4, respectively. At 13 and 75% moisture levels, pressure drop values of the wood chips were the highest. The lowest pressure drops were measured for the corn cobs, followed by the cobs with 5, 10, and 15% shale. At 13% moisture level, pressure drop values of the corn cobs were much smaller than previously reported pressure drop values of 6 month-old shredded wood (~0-1300 Pa/m) and 2 year-old wood chip (~0-1800 Pa/m) biofilters (Akdeniz and Janni, 2012).

Figure 3. Pressure drops per meter of media depth at 13% moisture content

Figure 4. Pressure drops per meter of media depth at 75% moisture content
Gas measurements

Hydrogen sulfide (H\textsubscript{2}S), ammonia (NH\textsubscript{3}), and N\textsubscript{2}O concentration ranges are shown in Table 4. Daily H\textsubscript{2}S and NH\textsubscript{3} percent reduction efficiencies of the cells are shown in Figures 5 and 6, respectively. Wood chips had the lowest percent reduction efficiencies. Corn cobs with 15% shale had the highest percent reduction efficiencies, followed by corn cobs with 10% shale and corn cobs with 5% shale. The average H\textsubscript{2}S and NH\textsubscript{3} percent reduction efficiencies of corn cobs with 15% shale were much higher than those of corn cobs without shale (cobs with 15% shale- H\textsubscript{2}S: 86.3%, NH\textsubscript{3}: 50.1%; cobs without shale-H\textsubscript{2}S: 13.3%, NH\textsubscript{3}: 11.7%). The high percent reduction efficiency of the cobs with shale was probably due to shale’s good moisture adsorption and desorption capacity.

Inlet and outlet N\textsubscript{2}O concentrations of the biofilter cells were close to each other and no N\textsubscript{2}O generation was observed even after water was added. Since an automated watering system was not used, a heavy rainfall event could not be simulated. In future studies, an automated watering system could be used to test N\textsubscript{2}O generation.

**Table 4: H\textsubscript{2}S, NH\textsubscript{3}, and N\textsubscript{2}O concentrations**

<table>
<thead>
<tr>
<th>Gases</th>
<th>Biofilter inlet (pit fan exhaust)</th>
<th>Wood chips outlet</th>
<th>Cobs outlet</th>
<th>Cobs with 5% shale outlet</th>
<th>Cobs with 10% shale outlet</th>
<th>Cobs with 15% shale outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH\textsubscript{3} (ppm)</td>
<td>19.2±6.8*</td>
<td>18.1±7.1</td>
<td>17.2±6.8</td>
<td>16.0±5.1</td>
<td>15.3±5.3</td>
<td>9.0±5.0</td>
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<tr>
<td></td>
<td>8.7-29.5**</td>
<td>8.0-28.5</td>
<td>7.4-25.8</td>
<td>7.5-24.5</td>
<td>3.1-23.8</td>
<td>1.1-19.7</td>
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<tr>
<td></td>
<td>n= 39***</td>
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<td>n= 39</td>
<td>n= 39</td>
<td>n= 39</td>
<td>n= 32</td>
</tr>
<tr>
<td>N\textsubscript{2}O (ppb)</td>
<td>700±81.7</td>
<td>702±81.7</td>
<td>698±78.8</td>
<td>715±88.4</td>
<td>710±86.4</td>
<td>709±84.2</td>
</tr>
<tr>
<td></td>
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<tr>
<td>H\textsubscript{2}S (ppb)</td>
<td>4069±1056</td>
<td>3733±1253</td>
<td>3589±1230</td>
<td>2729±1245</td>
<td>1938±822</td>
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<td>n= 42</td>
<td>n= 42</td>
<td>n= 35</td>
</tr>
</tbody>
</table>

*Averages of n day measurements ± standard deviations, **concentration ranges, ***n= number of days samples collected.*

**Figure 5.** Percent H\textsubscript{2}S reductions
Objective 3: To estimate the cost of using the diatomaceous shale as a biofilter media additive

There is no established market for corn cobs and diatomaceous shale. However, corn cobs are advertised for $50 per ton and the estimated price of diatomaceous shale is $20 per 20 kg bag. Based on this information, the cost of 0.9 m$^3$ corn cobs is $5.77. The corn cobs plus 15% shale costs $119. With 0.9 m$^3$ media, about 229 m$^3$ h$^{-1}$ (135 cfm) air was treated. The cost of corn cobs per air treated was less than $0.05. The cost of the corn cobs and the diatomaceous shale per air treated was $0.52 per m$^3$ h$^{-1}$ air treated or $0.88 per cfm air treated.

Discussion:

Diatomaceous shale used to control biofilter media moisture content had good adsorption capacity and superior desorption capacity unlike other adsorbents (e.g., activated carbon, diatomaceous earth, zeolite) reported in the literature. For this study wood chips had the lowest NH$_3$ and H$_2$S gas reduction efficiencies. Corn cobs with 15% shale had the highest gas reduction efficiencies, followed by corn cobs with 10% shale and corn cobs with 5% shale. The average H$_2$S and NH$_3$ percent reduction efficiencies of corn cobs with 15% shale were much higher than those of corn cobs without shale (cobs with 15% shale - H$_2$S: 86.3%, NH$_3$: 50.1%; cobs without shale - H$_2$S: 13.3%, NH$_3$: 11.7%). Inlet and outlet N$_2$O concentrations of the biofilter cells were close to each other and no N$_2$O generation was observed. In future studies, an automated watering system could be used to test N$_2$O generation under wet conditions. Corn cobs represent another commonly available and relatively low cost biofilter media for swine producers that have biofilters for treating air emissions from pit fans. A future study to determine corn cob useful life in a biofilter would improve the long term biofilter media cost estimate. Corn cob costs are not well established, using $50 per ton the estimated cost of the corn cob media with 15% diatomaceous shale was $0.52 per m$^3$ h$^{-1}$ air treated or $0.88 per cfm air treated. The corn cobs alone were less than $0.03 per m$^3$ h$^{-1}$ air treated or $0.05 per cfm air treated. Corn cobs with 15% diatomaceous shale had over five times higher gas reduction efficiencies compared to the corn cobs alone.
References


