MEASUREMENT AND MODELING OF EMISSIONS OF REDUCED SULFUR COMPOUNDS FROM CONCENTRATED ANIMAL FEEDING OPERATIONS

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1. INTRODUCTION

Emissions of reduced sulfur compounds (RSCs) into the atmosphere from concentrated animal feeding operations (CAFOs) are an environmental concern. RSCs are odorous and can therefore affect the quality of life for people in surrounding areas (Wing and Wolf, 2000) and have associated health impacts (Schiffman et al., 2005). RSCs can also have regional effects. RSCs can react to form sulfur dioxide (SO$_2$), which can then react to form aerosols such as ammonium sulfate and ammonium bisulfate. The formation of particulate matter can affect human health through damage to the lungs (McMurry et al., 2004), impair visibility (Seinfeld et al., 1998) and scatter incoming solar radiation, resulting in regional cooling (Lovelock et al., 1972). North Carolina is a state where CAFOs could have a potential effect on the environment. This is largely the result of the development of the hog industry. There are ~2600 hog CAFOs in North Carolina yielding a hog population of ~ 10 million. The majority of these hog farms are located in the southeastern coastal plain region of North Carolina.

RSCs are produced as hog manure decomposes anaerobically. Of the RSCs emitted from CAFOs, Hydrogen sulfide (H$_2$S) typically has the largest emissions. Therefore it has been the most extensively studied of the RSCs (e.g. Lim et al., 2003; Zahn et al., 2001; Zhu et al., 2000; Ni et al., 2002; Blunden and Aneja, 2008; Blunden et al., 2008).

Other RSCs have not been studied as extensively, with only a few studies reporting their concentrations at hog facilities (Clanton and Schmidt, 2000; Trabue et al., 2008; Blunden et al., 2005). Furthermore, there is only one known study (Kim et al., 2007), which has reported RSCs emission rates. However, this study focused on barn emissions rates. There are no known studies reporting anaerobic lagoon emission rates.

Due to different production, management and environmental conditions, it is important to develop regional CAFO emission factors. Therefore the objective of this research was to estimate RSC emissions from hog CAFOs in North Carolina by developing emission factors based on measured emissions. A further objective is to develop a process based model for H$_2$S, the largest RSC emitted from CAFOs. This will potentially enable H$_2$S emissions to be predicted from a variety of manure surfaces and in different production, management and environmental conditions.

This paper presents an overview of the measurement methodology, and focuses on the measurement of RSCs emissions to develop emission factors for estimating North Carolina RSC emissions. Additionally a brief summary of the development of H$_2$S process-based model is presented. More details on the process based model will be presented, once the analysis is completed. The effect of meteorological and physiochemical factors on RSCs lagoon and barn emissions will be discussed in another paper.

2. METHOD AND MATERIAL

2.1 Sampling Site

The sampling site is a commercial hog farm located in eastern North Carolina. The hog CAFO has eight mechanically ventilated finishing barns with a shallow pit recharge system. Each barn has a hog population between 900-1000. The waste treatment method employed by the majority of hog farms in North Carolina is known as ‘Lagoon and Spray Technology’ (LST). In this waste treatment method, the waste from the pigs falls through slatted floors into a shallow pit. This waste is flushed through pipes into an anaerobic treatment lagoon. The lagoon waste is recycled by being used to flush the barns. Also, the lagoon

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waste can be used to spray on crops as a source of nutrients.

### 2.2 Sampling Scheme

Measurements of RSCs were made from the anaerobic lagoon and the barn. Sampling was conducted over all four seasonal periods, the summer season from June 8th-28th, 2007; the fall season from the October 20th-November 12th, 2007; the winter season from February 8th-29th, 2008; and the spring season from April 11th-28th, 2008.

Lagoon measurements were made using a dynamic-flow through chamber system for an ~ one week sampling period. Barn measurements were also made from one of the barns for a period of ~ one week. Flux was measured by placing a sample line directly in front of a ventilation fan and measuring the fan flow rate using a rotation-voltage relationship system. H$_2$S concentrations were measured in-situ using a pulsed fluorescence H$_2$S/SO$_2$ analyzer. Other reduced sulfur compounds were collected using SUMMA and Fused Silica lined (FSL) canisters. These were analyzed ex-situ using Gas Chromatography-Flame Ionization Detection (GC-FID), which was coupled with a cryogenic trap to pre-concentrate samples. A GC-FID detects compounds with a hydrocarbon bond, which includes the RSCs of interest, methyl mercaptan (CH$_3$SH), dimethyl sulfide (DMS; CH$_3$SCH$_3$), and dimethyl disulfide (DMDS; CH$_3$S$_2$CH$_3$).

During lagoon measurements, continuous physicochemical measurements of lagoon temperature and pH were made at a depth of ~10 cm. Anaerobic lagoon samples were also collected and analyzed for total sulfide content. For barn measurements, the barn temperature was continuously measured at the fan outlet. The following meteorological parameters: air temperature, relative humidity, wind speed, wind direction and solar radiation were also measured throughout the sampling period.

### 3. RESULTS AND DISCUSSION

#### 3.1 Lagoon Emissions

RSC lagoon fluxes are presented in Table 1. The RSC of interest, methyl mercaptan is not presented, as the compound was not identified in any lagoon or barn samples. Canister stability test results showed methyl mercaptan to be highly reactive. Therefore it is hypothesized that this factor and low concentrations resulted in methyl mercaptan not being detected. A Gas Chromatography-Mass Spectrometer (GC-MS) additionally identified carbonyl sulfide (COS), and carbon disulfide (CS$_2$) in samples, but for this study, the GC-MS was not used to quantify compounds.

<table>
<thead>
<tr>
<th>Season</th>
<th>H$_2$S Flux (µg m$^{-2}$ min$^{-1}$)</th>
<th>DMS Flux (µg m$^{-2}$ min$^{-1}$)</th>
<th>DMDS Flux (µg m$^{-2}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer</td>
<td>3.82 (3.24) a N = 706b</td>
<td>0.26 (0.08) n = 10c</td>
<td>0.22 (0.04) n = 10d</td>
</tr>
<tr>
<td>Fall</td>
<td>1.17 (1.62)</td>
<td>0.11 (0.08) n = 10</td>
<td>0.04 (0.01) n = 10</td>
</tr>
<tr>
<td>Winter</td>
<td>0.08 (0.09) N = 631</td>
<td>0.05 (0.04) n = 11</td>
<td>0.02 (0.02) n = 11</td>
</tr>
<tr>
<td>Spring</td>
<td>0.27 (1.71) N = 479</td>
<td>0.06 (0.03) n = 10</td>
<td>0.11 (0.03) n = 10</td>
</tr>
<tr>
<td>Average</td>
<td>1.33</td>
<td>0.12</td>
<td>0.09</td>
</tr>
</tbody>
</table>

*a Mean value; b 1 Standard Deviation; c N represents the number of 15 minute averaged data points; d n is the number of canister samples collected

The H$_2$S lagoon fluxes range from 0.08 µg m$^{-2}$ min$^{-1}$ in the winter to 3.82 µg m$^{-2}$ min$^{-1}$ in the summer. Overall, the average H$_2$S flux over the four seasons is 1.33 µg m$^{-2}$ min$^{-1}$. In comparison, the average DMS and DMDS fluxes are at least an order of magnitude lower, 0.12 and 0.09 µg m$^{-2}$ min$^{-1}$, respectively. DMS flux ranged from 0.05-0.26 µg m$^{-2}$ min$^{-1}$, while DMDS ranged from 0.02-0.22 µg m$^{-2}$ min$^{-1}$. Similarly, DMS and DMDS have their highest and lowest fluxes in the summer and winter, respectively. Overall, the H$_2$S fluxes are similar to fluxes measured previously at the same sampling site (Blunden and Aneja, 2008), but are ~2 orders of magnitude lower than the previous studies from other parts of the U.S. (Lim et al., 2003; Zahn et al., 2001). This difference in flux values is hypothesized to be the influence of the total sulfide content of the waste. There are no known previous studies that have reported DMS and DMDS lagoon fluxes.
3.1.1 Emission factors

Emission factors for RSC lagoon emissions were calculated for each sampling season based on the lagoon surface area at the time of sampling. The lagoon surface area was only found to vary 6% throughout the sampling seasons, therefore the effects on relative seasonal fluxes were minimal. The average of the seasonal fluxes was used to determine RSCs lagoon emission factors. The lagoon emission factor was 34.2 g day\(^{-1}\) for H\(_2\)S. This was an order of magnitude higher than the DMS and DMDS lagoon emission factors, which were 3.09 and 2.54 g day\(^{-1}\), respectively.

3.2 Barn Concentrations and Emissions

Table 2 presents the concentrations and emissions for H\(_2\)S, DMS and DMDS. H\(_2\)S average seasonal concentrations range from 72 ppb in the summer to 631 ppb in the spring. The spring concentration is actually higher than reported, due to 27% of the concentration data being beyond the 1000 ppb detection limit of the H\(_2\)S=SO\(_2\) analyzer. The H\(_2\)S concentrations are 2-3 orders of magnitude higher than the DMS and DMDS concentrations. The DMS and the DMDS concentrations range from 0.17-0.89 ppb and 0.46-0.96 ppb, respectively. The highest seasonal concentrations for DMS and DMDS both occurred in the fall season. Similarly the lowest seasonal concentration both occur in the summer. The highest individual DMS concentration was 2.09 ppb, which occurred in the summer season. The highest individual DMDS concentration was 1.69 ppb, which was measured in the spring season.

Table 2. RSC barn concentration and emission rates

<table>
<thead>
<tr>
<th>Season</th>
<th>H(_2)S (ppb)</th>
<th>DMS</th>
<th>DMDS</th>
<th>H(_2)S (g day(^{-1}))</th>
<th>DMS</th>
<th>DMDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer</td>
<td>72(^a), 73(^b)</td>
<td>0.17</td>
<td>0.46</td>
<td>189</td>
<td>0.87</td>
<td>4.32</td>
</tr>
<tr>
<td></td>
<td>(43)(^c)</td>
<td></td>
<td>(0.21)</td>
<td>(0.37)</td>
<td>(42.4)</td>
<td>(0.86)</td>
</tr>
<tr>
<td></td>
<td>N(^d) = 518</td>
<td>n(^e) = 11</td>
<td>n = 11</td>
<td>N = 518</td>
<td>n = 11</td>
<td>n = 11</td>
</tr>
<tr>
<td>Fall</td>
<td>327, 307</td>
<td>0.89</td>
<td>0.96</td>
<td>206</td>
<td>2.17</td>
<td>3.90</td>
</tr>
<tr>
<td></td>
<td>(158)</td>
<td>(0.58)</td>
<td>(0.39)</td>
<td>(88.7)</td>
<td>(1.21)</td>
<td>(2.16)</td>
</tr>
<tr>
<td></td>
<td>N = 741</td>
<td>n = 11</td>
<td>n = 11</td>
<td>N = 741</td>
<td>n = 11</td>
<td>n = 11</td>
</tr>
<tr>
<td>Winter</td>
<td>164, 150</td>
<td>0.83</td>
<td>0.62</td>
<td>79.8</td>
<td>1.07</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td>(63)</td>
<td>(0.39)</td>
<td>(0.34)</td>
<td>(53.6)</td>
<td>(0.49)</td>
<td>(0.99)</td>
</tr>
<tr>
<td></td>
<td>N = 507</td>
<td>n = 10</td>
<td>n = 10</td>
<td>N = 507</td>
<td>n = 10</td>
<td>n = 10</td>
</tr>
<tr>
<td>Spring</td>
<td>631(^f), 645</td>
<td>0.59</td>
<td>0.52</td>
<td>647 (^f)</td>
<td>1.51</td>
<td>1.87</td>
</tr>
<tr>
<td></td>
<td>(240)</td>
<td>(0.23)</td>
<td>(0.47)</td>
<td>(219)</td>
<td>(0.47)</td>
<td>(1.23)</td>
</tr>
<tr>
<td></td>
<td>N = 649</td>
<td>n = 11</td>
<td>n = 11</td>
<td>N = 649</td>
<td>n = 11</td>
<td>n = 11</td>
</tr>
</tbody>
</table>

\(^a\) Mean value; \(^b\) Average daily mean value; \(^c\) 1 standard deviation; \(^d\) N represents the number of 15 minute averaged data points; \(^e\) n is the number of canister samples collected; \(^f\) 27% of the 15 minute averaged data points, had at least one minute average above the limit of detection of the analyzer

The term ‘odor threshold’ is defined as the concentration of a chemical compound at which its odor can first be detected. A summary of H\(_2\)S, DMS, and DMDS odor thresholds and characteristics are presented in Table 3.

Table 3. RSCs odor thresholds and characteristics

| Odor Threshold (ppb) | Odor Characteristic
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)S</td>
<td>17.8(^a) 1-130(^b) 4.5(^c) 8.1(^d)</td>
</tr>
<tr>
<td>DMS</td>
<td>2.24(^e) 9.8-20(^f)</td>
</tr>
<tr>
<td>DMDS</td>
<td>12.3(^g) 0.78-3.6(^h)</td>
</tr>
</tbody>
</table>

\(^a\) Devos et al., (2002); \(^b\) Haz-Map, (2009); \(^c\) American Industrial Hygiene Association,(1989); \(^d\) Rychlik et al.,(1998) ; \(^e\) Odor characteristic from Schiffman et al., (2001)
For H$_2$S, the highest odor threshold (130 ppb) is exceeded in all seasons with 71% of 15 minute average concentrations exceeding this odor threshold. The average seasonal concentration exceeds this odor threshold for three of the four sampling seasons. H$_2$S concentrations are generally one to two orders of magnitude higher than the odor threshold, depending on which reported odor threshold you compare to. No DMS concentrations exceeded their reported odor thresholds. Individual DMDS concentrations exceed the lower limit of the odor threshold range reported by Haz-Map, (2009) in all sampling seasons. The fall average concentration was the only average seasonal concentration to exceed this value.

The H$_2$S seasonal barn emission rates (Table 2) range from a high of 647 g day$^{-1}$ in the spring season, to a low of 79.8 g day$^{-1}$ in the winter season. DMS and DMDS emission rates were two to three orders of magnitude lower than H$_2$S emission rates. DMDS emission rates were higher than DMS emission rates in all sampling seasons.

### 3.2.1 Barn emission factors

Animal weight can potentially influence emissions rates from a barn. Measured emissions were normalized by 500 kg of live animal weight (LAW), also known as 1 animal unit (AU). The pig production numbers, the calculated LAW and the normalized RSC emission factors are shown in Table 4.

<table>
<thead>
<tr>
<th>Sampling Season</th>
<th>Number of Pigs</th>
<th>Number of weeks in rotation</th>
<th>Average Weight (kg)</th>
<th>Total Live Animal Weight (kg)</th>
<th>Normalized Emission Factor (g day$^{-1}$ AU$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summer</td>
<td>884.5</td>
<td>7-8</td>
<td>48.7</td>
<td>43,049</td>
<td>2.20 0.010 0.050</td>
</tr>
<tr>
<td>Fall</td>
<td>994.5</td>
<td>4-5</td>
<td>34.6</td>
<td>34,428</td>
<td>2.99 0.032 0.056</td>
</tr>
<tr>
<td>Winter</td>
<td>476</td>
<td>20-21</td>
<td>116.6</td>
<td>55,513</td>
<td>0.72 0.010 0.011</td>
</tr>
<tr>
<td>Spring</td>
<td>874.5</td>
<td>8-9</td>
<td>50.6</td>
<td>44,262</td>
<td>7.31 0.017 0.021</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.3 0.017 0.035</td>
</tr>
</tbody>
</table>

The average normalized H$_2$S emission factor (3.3 g day$^{-1}$ AU$^{-1}$) is approximately two orders of magnitude higher than DMS (0.017 g day$^{-1}$ AU$^{-1}$) and DMDS (0.035 g day$^{-1}$ AU$^{-1}$). H$_2$S seasonal normalized emission factors ranged from 0.72 g day$^{-1}$ AU$^{-1}$ in the winter to 7.31 g day$^{-1}$ AU$^{-1}$ in the spring. The highest seasonal DMS and DMDS emission factors were both in the fall with values of 0.032 and 0.056 g day$^{-1}$ AU$^{-1}$, respectively. The average concentrations and emissions in this study are of a similar magnitude to a previous study at the same sampling site (Blunden et al., 2008), and other studies in the U.S. (Zhu et al., 2000; Ni et al., 2002), despite differences in production, management and environmental conditions.

### 3.3 North Carolina RSC Emission Factors

North Carolina lagoon emissions were estimated by calculating the total lagoon area in North Carolina. A previous study estimated using a spot satellite image that the average size of a lagoon is ~1 ha (Aneja et al., 2000). The number of hog farms in North Carolina is ~2600. Therefore by using the lagoon emission factors for the RSCs, the total North Carolina emissions from swine lagoons are ~18,312 kg yr$^{-1}$ for H$_2$S, ~1640 for DMS and ~1230 kg yr$^{-1}$ for DMDS. The North Carolina barn emissions were estimated using statistics provided by the United States Department of Agriculture (USDA, 2009), which has information on the number and weight of North Carolina hogs. From this a total live animal weight of ~0.61 billion lbs was calculated for North Carolina. By applying the normalized emission factor, it is estimated that North Carolina hog barns emit ~1.45 million kg yr$^{-1}$ of H$_2$S. Estimated North Carolina emissions of DMS and DMDS were considerably lower, ~7481 kg yr$^{-1}$ and ~15,401 kg yr$^{-1}$, respectively. In comparison, North Carolina H$_2$S barn emissions are two orders of magnitude higher than lagoon emissions. For DMS and DMDS, barn emissions are not as dominant, with lagoon emissions contributing ~22% and ~8% of total emissions, respectively.
Total emissions from North Carolina hog farms (barn + lagoon) are therefore \(1.48 \text{ million kg yr}^{-1}\) for \(\text{H}_2\text{S}\), \(9120 \text{ kg yr}^{-1}\) for DMS, and \(16631 \text{ kg yr}^{-1}\) for DMDS.

The North Carolina Division of Air Quality (NCDAQ) released an North Carolina \(\text{H}_2\text{S}\) emission inventory for 2003 stating total emissions of \(11.9 \text{ million lbs yr}^{-1}\) (NCDAQ, 2003). This inventory did not include emissions from animal operations. By assuming that the \(\text{H}_2\text{S}\) emission inventory has remained constant and adding the contribution of the hog farms to the inventory, it is estimated that \(\text{H}_2\text{S}\) emissions from hog farms in North Carolina comprise \(22\%\) of statewide \(\text{H}_2\text{S}\) emissions.

4. MODELING OF \(\text{H}_2\text{S}\) EMISSIONS

The largest RSC emitted from CAFOs is \(\text{H}_2\text{S}\). These emissions though vary with production, management and environmental conditions. Therefore there is a need for a process based model, which will provide a method for quantifying \(\text{H}_2\text{S}\) manure emissions in different production, management and environmental conditions.

A process based air-surface interface mass transfer model with chemical reactions was developed based on theoretical principles and related published information on \(\text{H}_2\text{S}\) emissions. Different approaches were used to calculate the three main components of the model: the Henry’s law constant, the dissociation constant, and the overall mass transport coefficient. The Henry’s law constant was calculated based on thermodynamic principles. Similarly, the dissociation constant was also calculated based on thermodynamic principles and was additionally corrected for the ionic strength of the manure. The overall mass transfer coefficient was estimated by using a previous study’s experimental results (Arogo et al., 1999). They considered the most important properties affecting mass transport to be the diffusivity of \(\text{H}_2\text{S}\) in air, the air viscosity, and the air density. By modeling these parameters using dimensional analysis, they identified the variables that needed to be measured to determine the relevant constant and exponents values. By using this study’s results, an appropriate overall mass transfer coefficient was developed.

Sensitivity analysis of the process based air-surface interface mass transfer model showed predicted fluxes to be most dependent on manure sulfide concentration and manure pH, and to a smaller extent on wind speed and manure temperature. The model predicted fluxes are being compared with the \(\text{H}_2\text{S}\) lagoon flux measurements described in this paper. Preliminary analysis shows model predicted fluxes to compare well to measured flux values. Future work will include further evaluation of the model by continuing to compare the predicted emissions to the measured lagoon emissions described in this paper. The aim is to develop a model which can be used to predict \(\text{H}_2\text{S}\) emissions from a variety of manure surfaces, thus allowing a method for quantifying emissions in different production, management and environmental conditions.

5. CONCLUSIONS

RSCs concentrations and emissions were measured from a hog CAFO in North Carolina. The average seasonal lagoon \(\text{H}_2\text{S}\) flux was \(1.33 \mu\text{g m}^{-2} \text{min}^{-1}\). DMS and DMDS fluxes were an order of magnitude lower, \(0.12\) and \(0.09 \mu\text{g m}^{-2} \text{min}^{-1}\), respectively.

Average \(\text{H}_2\text{S}\) seasonal barn emissions were \(3.3 \text{ g day}^{-1} \text{ AU}^{-1}\), which was approximately two orders of magnitude higher than those for DMS and DMDS, \(0.017 \text{ g day}^{-1} \text{ AU}^{-1}\) and \(0.035 \text{ g day}^{-1} \text{ AU}^{-1}\), respectively.

Using the lagoon and barn emission factors, it was calculated that total emissions from North Carolina hog farms are \(1.48 \text{ million kg yr}^{-1}\) for \(\text{H}_2\text{S}\), \(9120 \text{ kg yr}^{-1}\) for DMS, and \(16631 \text{ kg yr}^{-1}\) for DMDS. It is estimated that North Carolina \(\text{H}_2\text{S}\) emissions from hog CAFOs comprise \(22\%\) of statewide \(\text{H}_2\text{S}\) emissions.

A process based air-surface interface mass transfer model with chemical reactions was developed based on theoretical principles and related published information on \(\text{H}_2\text{S}\) emissions. Preliminary analysis shows model predicted fluxes to be comparing well to measured flux values. The model will be continued to be evaluated by comparing the predicted emissions to the measure lagoon emissions in this study.

6. ACKNOWLEDGEMENTS

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