

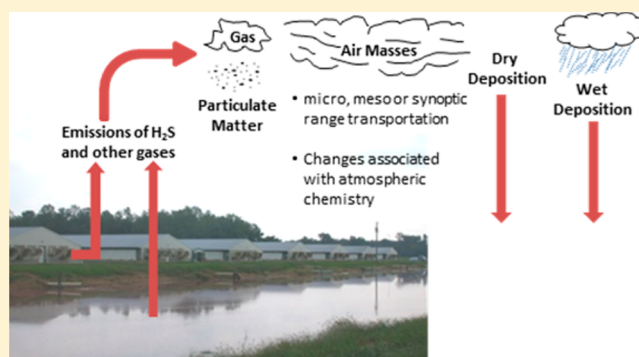
Measurement and Modeling of Hydrogen Sulfide Lagoon Emissions from a Swine Concentrated Animal Feeding Operation

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S Supporting Information

ABSTRACT: Hydrogen sulfide (H₂S) emissions were determined from an anaerobic lagoon at a swine concentrated animal feeding operation (CAFO) in North Carolina. Measurements of H₂S were made continuously from an anaerobic lagoon using a dynamic flow-through chamber for ~1 week during each of the four seasonal periods from June 2007 through April 2008. H₂S lagoon fluxes were highest in the summer with a flux of $3.81 \pm 3.24 \mu\text{g m}^{-2} \text{min}^{-1}$ and lowest in the winter with a flux of $0.08 \pm 0.09 \mu\text{g m}^{-2} \text{min}^{-1}$. An air-manure interface (A-MI) mass transfer model was developed to predict H₂S manure emissions. The accuracy of the A-MI mass transfer model in predicting H₂S manure emissions was comprehensively evaluated by comparing the model predicted emissions to the continuously measured lagoon emissions using data from all four seasonal periods. In comparison to this measurement data, the A-MI mass transfer model performed well in predicting H₂S fluxes with a slope of 1.13 and an *r*² value of 0.60, and a mean bias value of $0.655 \mu\text{g m}^{-2} \text{min}^{-1}$. The A-MI mass transfer model also performed fairly well in predicting diurnal H₂S lagoon flux trends.



1. INTRODUCTION

The intensification of animal agriculture to meet the food demands of an increasing world population has resulted in an increase in concentrated animal feeding operations (CAFOs). CAFOs emit nitrogen, sulfur, volatile organic compounds, and particulate matter into the atmosphere.¹ In North Carolina, there is a swine population of ~9 million,² of which the vast majority are housed in swine CAFOs.

The main sulfur compound emitted from CAFOs is hydrogen sulfide (H₂S), which is a colorless, potentially harmful gas,³ with an odor characteristic described as “rotten eggs”.⁴ H₂S emissions occur from animal waste as a result of anaerobic microbial decomposition of sulfate. CAFO emissions of odorous compounds such as H₂S are important as they can result in health symptoms and furthermore health effects,⁵ and affect the quality of life for people in the surrounding area.^{6–8} As a result of oxidation and subsequent reactions, H₂S emissions can result in particulate matter formation.⁹ Particulate matter in the form of PM_{fine} (particulate matter with an aerodynamic diameter equal or less than 2.5 μm) has been associated with adverse health effects including premature mortality.¹⁰ Particulate matter can also additionally impair visibility^{11,12} and scatter incoming solar radiation resulting in regional cooling.¹³

There have been less than a handful of studies that have measured H₂S emissions from swine lagoons.^{14–16} Therefore, further measurements are needed to assess the magnitude of

H₂S emissions and the effects of production, management, and environmental conditions. This study continues and builds upon the work of Blunden and Aneja¹⁶ by measuring an additional four seasons of H₂S lagoon emissions at the same commercial swine farm in eastern North Carolina. This provides two sets of seasonal measurements at the same swine CAFO, allowing a comprehensive analysis of seasonal H₂S lagoon flux trends as well as allowing a comprehensive assessment of H₂S lagoon fluxes at this swine CAFO in comparison to previous swine CAFO lagoon studies in different locations. This manuscript presents the H₂S lagoon emissions from the four sampling seasons and evaluates them with respect to diurnal and seasonal variations. The effects of meteorological and physicochemical parameters are also evaluated, using a more robust statistical approach than that provided in the Blunden and Aneja¹⁶ study.

Making accurate measurements of H₂S emissions from swine CAFOs is expensive, therefore there is a need to develop process-based models which can account for the different environmental conditions at each swine CAFO. There are a few studies that have modeled H₂S swine manure emissions.^{17–19} However, of these previous studies, none have developed an

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accurate H₂S emission model in terms of predicting the magnitude and the diurnal trends associated with the influence of environmental factors. Furthermore, the models in these previous studies were not comprehensively evaluated with respect to seasonal variations. Blunden et al.¹⁷ developed three different H₂S emission models which had different assumptions for the mass transfer of H₂S from waste. In comparison to emission measurements from an anaerobic lagoon, modeled emissions showed a reasonable prediction of the influence of environmental factors on H₂S diurnal trends, but overestimated emission rates, sometimes by up to 2 orders of magnitude. Blanes-Vidal et al.^{18,19} developed a Gas Emission (GE)-pH coupled model which modeled the emissions of four gases including H₂S from swine waste. The gas emission sub-model they developed was similar to that developed by Blunden et al.¹⁷ and was coupled with a pH buffer sub-model, which predicts surface pH based on volatilization of gases. In comparison to measurement data, the predicted fluxes from the GE-pH model performed fairly well in terms of magnitude of H₂S emissions,^{18,19} but only performed moderately in predicting H₂S diurnal emission trends. Furthermore, the evaluation period for the H₂S diurnal emission trends was limited, as emission trends were only compared over a 24 h period. Due to limited empirical data available at the time of these previous models development, the performance of the models may be influenced by inaccuracies in the determination of the mass transfer rate of H₂S from the swine manure into the atmosphere. This manuscript describes the development of a process-based air-manure interface (A-MI) mass transfer model, which uses the results from a recently published experimental study by Santos et al.²⁰ to develop a more representative H₂S mass transfer rate. The accuracy of the A-MI mass transfer model in predicting H₂S manure emissions is evaluated by comparing the model predicted emissions to the measured lagoon emissions and are comprehensively evaluated with respect to seasonal and diurnal variations.

As well as accounting for environmental conditions, there is a need to model H₂S CAFO emissions for different manure types, and production and management conditions. Therefore, a similar approach to the Montes et al.²¹ study was adopted for two of the main components (dissociation constant and Henry's law constant) of the A-MI mass transfer model. This approach develops the dissociation constant and the Henry's law constant based on thermodynamic principles, which allows modification for the ionic properties of the manure, therefore these model components can account for different manure types and production and management conditions as well as potentially being applied to other gases of interest.

2. METHOD AND MATERIALS

2.1. Hydrogen Sulfide Lagoon Emission Measurements.

2.1.1. Sampling Site. The sampling site was a commercial swine CAFO located in eastern North Carolina. At the swine CAFO, there are eight finishing barns with typically between 900 and 1000 pigs in each barn. Generally, the pigs weigh between 20 and 24 kg on arrival, and stay at the barn for 16–20 weeks. The barns are mechanically ventilated. The swine CAFO uses a conventional waste management method, known as “lagoon and spray technology”, which is used by the majority of swine CAFOs in North Carolina. A description of the waste management method is provided in the Supporting Information, SI.

2.1.2. Sampling Scheme. Measurements of H₂S emissions were made during all four seasonal periods from June 2007 through April 2008. Lagoon emission measurements were made for a ~1 week period during each sampling season. Sampling was conducted during the summer season from June 8th to June 21st, 2007; the fall season from the October 20th to November 2nd, 2007; the winter season from February 18th to February 29th, 2008; and the spring season from April 11th to April 16th, 2008.

2.1.3. Lagoon H₂S Flux Measurements and Instrumentation. Anaerobic lagoon flux was determined using a dynamic flow-through chamber system.^{16,22,23} A description of the dynamic flow-through chamber system and H₂S lagoon flux measurements are provided in the SI. A Thermo Environmental Instrument (TEI) model 450C pulsed fluorescence H₂S/SO₂ analyzer (Thermo Environmental Corporation, Mountain View, CA) was used to continuously measure H₂S concentrations. It should be noted that SO₂ concentrations were not analyzed at the swine CAFO, as concentrations were negligible. A further description of the TEI instrument and its QA/QC procedures are provided in the SI.

2.1.4. Lagoon and Meteorological Parameter Measurements. Lagoon temperature (CS107: Campbell Scientific Inc., Logan, UT) and lagoon pH (CSIM11: Campbell Scientific Inc.) were measured continuously ~7 cm below the lagoon surface. The pH probe was placed in buffer solution and calibrated before and after each sampling period. Meteorological measurements were made using a meteorological tower. Measurements of relative humidity (RH) and air temperature (CS500-L Vaisala 50Y; Campbell Scientific Inc.) as well as solar radiation (LI200X; Campbell Scientific Inc.) were made at a height of 2 m. In addition, measurements of wind speed and wind direction (034-B Windset, Met One Instruments; Campbell Scientific, Inc.) were made at a height of 10 m. The meteorological tower was ~6 m from the lagoon edge and on average 10 m from the dynamic flow-through chamber. Near-surface (<10 cm) anaerobic treatment lagoon samples were taken daily to be analyzed for sulfide content. The lagoon samples were preserved for sulfide analysis by adding 1 mL of 2N zinc acetate and ~6N NaOH until the pH > 9. The samples were stored below 4 °C until analysis. Samples were analyzed within 5 days of collection at the North Carolina Division of Water Quality. Sulfide content was measured using color metric analysis, using Standard Method 4500-S2-D.²⁴

A CR23X data logger and a CR10X data logger (Campbell Scientific, Inc.) were used to collect and record data. The data loggers were kept inside a temperature controlled mobile laboratory.

2.2. Modeling of H₂S Manure Emissions. A process based air-manure interface (A-MI) mass transfer model was developed to model H₂S manure emissions. Gas mass transfer models are typically based on the two film theory, where the flux from the bulk liquid phase to the bulk gas phase is related to the molecular exchange of gases between water and gas films.^{25,26} A diagram of the two-film model is presented in the SI. For this study, the bulk liquid phase is approximated as representing manure. The resistance to the mass transfer of a gas, in this case H₂S, from bulk manure phase to the bulk gas phase is from interfacial liquid and gas films. The combined resistance to mass transfer is termed the overall mass transfer coefficient (K_m). The influence of the resistance to mass transfer can be approximated by the representation of H₂S concentration [H₂S], which decreases from the bulk manure

phase ($[H_2S_{mn}]$) through the manure interface ($[H_2S_{mni}]$) and gas interface ($[H_2S_{gi}]$) to the bulk gas phase ($[H_2S_g]$). The equilibrium between the H_2S in the liquid and gas phase is expressed by the Henry's law constant (H_L), which determines the equilibrium concentration. By assuming that the H_2S gas concentration in ambient air ($[H_2S_g]$) is of small magnitude in comparison to the concentration of H_2S in the bulk manure phase and thus can be neglected, the H_2S flux from the manure is determined using the following equation:

$$J_{H_2S} = K_m[H_2S]_{mn}H_L \quad (1)$$

where J_{H_2S} is the H_2S flux ($\mu\text{g m}^{-2} \text{min}^{-1}$), K_m is the overall mass transfer coefficient, and $[H_2S]_{mn}$ is the concentration of H_2S in the bulk manure phase. The concentration of H_2S in the bulk manure phase is determined by the following:

$$[H_2S]_{mn} = (\text{TSC})(f_{H_2S}) \quad (2)$$

where TSC is the total sulfide concentration and f_{H_2S} is the fraction of the TSC that is H_2S . Aqueous H_2S exists in equilibrium with the bisulfide anion (HS^-) and sulfide anion (S^{2-}). The pH of the liquid constituent determines the dissociation and thus the fraction of the three sulfide species that are available (a figure presenting this relationship is presented in the SI).²⁷ Between a pH of 5–9, the fraction of H_2S available decreases as the pH increases due to dissociation into HS^- . Thus the lower the pH, the more H_2S there is available to be transferred from the lagoon into the atmosphere. Therefore f_{H_2S} is determined by the following equation:

$$f_{H_2S} = \frac{10^{-\text{pH}}}{10^{-\text{pH}} + K_d} \quad (3)$$

where K_d is the dissociation constant.

The following sections will describe how K_m , K_d , and H_L are determined. As mentioned, the H_2S emission model was developed with the aim of being used to predict emissions from a variety of manure surfaces, therefore a similar approach to the Montes et al.²¹ study was adopted for the development of K_d and H_L . This approach involves determining expressions for these variables based on thermodynamic principles and then modifying these expressions based on the properties of the manure.

2.2.1. Overall Mass Transfer Coefficient. In this study, an expression for the overall mass transfer coefficient (K_m) was developed based on a recent experimental study by Santos et al.,²⁰ which made measurements of the H_2S overall mass transfer coefficient from distilled water using a wind tunnel. The study determined the overall mass transfer coefficient while making simultaneous measurements of environmental parameters including friction velocity (U^*), relative humidity (RH), absolute humidity (AH), temperature of the liquid (T_L), and air temperature (T_{air}). The Santos et al.²⁰ study was selected as it is the most representative empirical study of the H_2S overall mass transfer coefficient currently available in literature. There is no other known experimental study that has measured the H_2S overall mass transfer coefficient using a wind tunnel, thus ensuring accurate simulation of the atmospheric boundary layer. Without the availability of the Santos et al.²⁰ study, previous H_2S manure modeling studies^{17–19} have modeled the mass transfer of H_2S using liquid and gas mass transfer coefficients based on studies using volatile organic compounds,^{28–30} and the diffusivity of H_2S in water.^{31–33} This

may lead to possible errors as H_2S may act differently to VOCs and there is likely to be a difference in the diffusivity of H_2S in water in comparison to manure.

As mentioned, the Santos et al.²⁰ study made measurements of the overall mass transfer coefficient and corresponding environmental parameters. However, an expression describing the variance of the overall mass transfer coefficient with respect to environmental parameters was not developed. Therefore, a statistical observation model based on the Santos et al.²⁰ experimental results (data provided in table in SI) was developed. Statistical analysis was performed using JMP (Statistical analysis software v7, Cary, NC). Multiple linear regression analysis, using forward stepwise regression was used to determine the best-fitting model. From this, the statistical observational model for K_m was determined to be the following:

$$K_m = -3.121 \times 10^{-6} - 4.277 \times 10^{-7}(T_{\text{air}}) + 7.3154 \times 10^{-7}(T_L) + 1.6659 \times 10^{-5}(U^*) \quad (4)$$

where K_m is in units of ms^{-1} , T_{air} is the air temperature in units of $^\circ\text{C}$, T_L is the liquid temperature in units of $^\circ\text{C}$, and U^* is the friction velocity in units of ms^{-1} . The statistical observational model has an r^2 value of 0.60 ($n = 14$) ($p = 0.02$). Equation 4 indicates that increasing air temperature will decrease the overall mass transfer coefficient and that increasing lagoon temperature and friction velocity will increase the overall mass transfer coefficient. Explanations for the influence of these environmental parameters on the overall mass transfer coefficient are provided in the SI. In this study, measurements of wind speed were made at a height of 10 m. To convert this wind speed to friction velocity to use in eq 4, the following equation was used:^{30,34}

$$U^* = 0.01U_{10}(6.1 + 0.63U_{10})^{0.5} \quad (5)$$

where U_{10} is the wind speed at a height of 10 m.

A correction factor of 0.6 was applied to the calculation of the overall mass transfer coefficient based on a study by Yongsiri et al.,³⁵ which determined that the H_2S overall mass transfer coefficient in sewer wastewater was 40% less than in deionized water.

2.2.2. Henry's Law Constant (H_L). Henry's law quantifies the equilibrium of H_2S at the manure surface interface to the air interface. In this study, the Henry's law constant (H_L) was based on a value of 0.105 M atm⁻¹ for H_2S ,³⁶ which is equal to 0.389 in dimensionless form (gas concentration/aqueous concentration (g/aq)) at 298.15 K. The Henry's law constant is a function of temperature. The effect of manure temperature on the Henry's law constant is taken into account by using the Van't Hoff equation.^{27,36,37} From this the following expression is obtained for H_L :

$$\log(H_L) = \log\left(0.389 \frac{298.15}{T}\right) - \left(\frac{\Delta H^\circ}{\ln(10)R} \left(\frac{1}{T} - \frac{1}{298.15}\right)\right) \quad (6)$$

where ΔH° is the enthalpy change for H_2S between gas and aqueous phase, which is 19.12 kJ mol⁻¹,³⁶ R is the universal gas constant (0.008314 kJ mol⁻¹ K⁻¹), and T is the manure temperature (K). This equation includes a temperature ratio for the variance of the dimensionless Henry's law constant.

Table 1. Lagoon H₂S Fluxes and Corresponding Environmental Parameters

season	H ₂ S flux (μg m ⁻² min ⁻¹)	lagoon temperature (°C)	lagoon pH	air temperature (°C)	wind speed (m s ⁻¹)	sulfide concentration (mg L ⁻¹)
Summer	3.81 ^a (3.24) ^b N = 705 ^c	25.89 (2.74) N = 676	7.26 (0.12) N = 520	21.91 (4.90) N = 705	1.45 (1.00) N = 552	1.50 ^d (1.87) n = 12 (8) ^e
Fall	1.17 (1.62) N = 646	20.54 (2.91) N = 645	7.52 (0.10) N = 559	17.81 (6.43) N = 646	1.68 (1.69) N = 646	1.10 (1.27) n = 12 (9)
Winter	0.08 (0.09) N = 631	12.23 (2.14) N = 605	8.02 (0.14) N = 631	6.97 (5.73) N = 631	2.05 (1.19) N = 631	1.32 (1.21) n = 12 (6)
Spring	0.27 (1.71) N = 478	19.93 (2.09) N = 478	8.03 (0.10) N = 469	14.45 (6.81) N = 469	2.76 (1.74) N = 469	0.85 (0.49) n = 10 (7)

^aMean value. ^b±1 Standard Deviation. ^cN represents the number of 15 min averaged data points. ^dSeasonal sulfide concentrations were calculated using a 1/2 detection limit value (0.5 mg L⁻¹), when samples concentrations were determined to less than the detection limit of 1 mg L⁻¹. ^eNumber of anaerobic lagoon samples collected, number in parentheses represent the number of samples at detection limit of 1 mg L⁻¹.

Equation 6 determines that the Henry's law constant increases as manure temperature increases.

2.2.3. Dissociation Constant. The dissociation constant (K_d) relates the equilibrium between H₂S and HS⁻ as follows:



Calculations for the H₂S dissociation in water were made using thermodynamic estimates of standard Gibbs free energy and standard enthalpy at 298 K.³⁶ The dissociation constant is also a function of temperature. Similarly to the Henry's law constant, the effect of temperature on the dissociation constant is described using the Van't Hoff equation. Using this, the following expression was obtained for the dissociation constant (K_d):

$$\log(K_d) = -6.99 - \left(\frac{\Delta H^\circ}{\ln(10)R} \left(\frac{1}{T} - \frac{1}{298.15} \right) \right) \quad (8)$$

where ΔH° is the enthalpy change for the dissociation of H₂S which is 22.15 kJ mol⁻¹,³⁶ R is the universal gas constant (0.008 314 kJ mol⁻¹ K⁻¹), and T is the manure temperature (K). Equation 8 determines that as temperature increases, the H₂S dissociation constant also increases.

2.2.4. Modification of Henry's Law Constant and Dissociation Constant for Ionic Properties of the Manure. As mentioned, the Henry's law constant and dissociation constant were calculated based on thermodynamic estimates of H₂S and HS⁻ in pure water, which does not contain any ions. However, in manure there are ions which will interact with H₂S and HS⁻, thus affecting the Henry's law constant (eq 6) and the dissociation constant (eq 7). To account for this interaction, a modified Henry's law constant (H_L^m) and dissociation constant (K_d^m) were calculated using a methodology developed by Montes et al.,²¹ which determines the effect of interaction of the species with other ions in the manure by calculating the activity coefficient of the species. Therefore, H_L^m and K_d^m are determined using the following equations:³⁷

$$H_L^m = \frac{H_L}{\gamma_{\text{H}_2\text{S}_{\text{manure}}}} \quad (9)$$

$$K_d^m = K_d \frac{\gamma_{\text{H}_2\text{S}_{\text{manure}}}}{\gamma_{\text{HS}^-_{\text{manure}}}} \quad (10)$$

where $\gamma_{\text{H}_2\text{S}_{\text{manure}}}$ and $\gamma_{\text{HS}^-_{\text{manure}}}$ are the activity coefficients for H₂S and HS⁻, respectively.

Activity coefficients were calculated using different equations for charged and neutral species. For HS⁻, the activity coefficient was calculated using the Davies equation:³⁶

$$\log \gamma_{\text{HS}^-} = -0.5(C^2) \left(\frac{I^{1/2}}{1 + I^{1/2}} - 0.3I \right) \quad (11)$$

where I is the ionic strength of the manure (mol L⁻¹) and c is the charge value of the ion (e.g., $c = 1$ for HS⁻) For H₂S, the activity coefficient was calculated using the following equation that is suggested for use with neutral molecules:³⁷

$$\log \gamma_{\text{H}_2\text{S}} = 0.1I \quad (12)$$

I is a function of electrical conductivity (EC) of the manure and is calculated using the following equation:²⁷

$$I = 0.016(\text{EC}) \quad (13)$$

where the EC of the manure is measured in units of mmhos cm⁻¹. For this study, average electrical conductivity measurements were obtained from a North Carolina swine anaerobic lagoon liquid characteristics database.³⁸ The average manure conductivity of 153 samples was 4.612 mmhos cm⁻¹, resulting in an ionic strength of 0.074 mol L⁻¹.

By substituting the values for the ionic strength of the manure, into eq 11 and eq 12, the activity coefficients and thus K_d^m and H_L^m were calculated. K_d^m was ~27% larger than K_d due to interaction with other ions and H_L^m was ~2% smaller than H_L due to interaction with other ions. The small difference in the Henry's Law constant between water and manure is supported by studies by Yongsiri et al.³⁵ and Al-Haddad et al.³⁹ Both these studies found that there was no significant difference in the Henry's law constant between water and municipal sewage wastewater.

3. RESULTS AND DISCUSSION

3.1. Lagoon Flux. **3.1.1. Seasonal Fluxes.** Seasonal H₂S lagoon fluxes and their corresponding environmental parameters are summarized in Table 1. Of the four seasons, the H₂S flux was highest during the summer season with an average flux value of 3.81 μg m⁻² min⁻¹. The second highest flux was measured in the fall season with a value of 1.17 μg m⁻² min⁻¹. The lowest fluxes were in the spring and winter, 0.27 and 0.08 μg H₂S m⁻² min⁻¹, respectively. The seasonal pH averages varied, with the lowest pH occurring in the summer (7.26). The pH was higher in the fall season with a value of 7.52. The highest seasonal pH averages were in the winter and spring with values of 8.02 and 8.03, respectively. Seasonal sulfide concentrations were fairly constant (0.85–1.50 mg L⁻¹), however, it should be noted that ~two-thirds of the samples were assigned a half detection limit value (0.5 mg L⁻¹) as they were below the limit of detection of 1 mg L⁻¹.

H₂S swine CAFO lagoon fluxes have been determined by other studies around the U.S. A summary of the H₂S lagoon fluxes and corresponding environmental parameters from this study and the previous lagoon flux studies are presented in

Table 2. H₂S Fluxes from Previous Swine CAFOs Lagoon Studies

reference	location	sampling period	lagoon temperature (°C)	pH	sulfide concentration (mg L ⁻¹)	H ₂ S flux (μg m ⁻² min ⁻¹)
Zahn et al. ¹⁴	MO	August	-	8.1	15	438
Zahn et al. ¹⁴	MO	September	-	8.2	17	492
Zahn et al. ¹⁴	MO	October	-	8.1	18	1266
Lim et al. ¹⁵	Midwest ^a	April–July	25	8.1	-	546
Lim et al. ¹⁵	Midwest ^a	April–July	25	7.9	-	138
Blunden and Aneja ¹⁶	NC	October–November	18	8.1	0.6	0.3
Blunden and Aneja ¹⁶	NC	February	12	8.1	3.2	~0.0
Blunden and Aneja ¹⁶	NC	April	15	8.1	1.8	0.5
Blunden and Aneja ¹⁶	NC	June	30	8.0	9.2	5.3
this study	NC	June	26	7.3	1.5	3.8
this study	NC	October–November	21	7.5	1.1	1.2
this study	NC	February	12	8.0	1.3	0.1
this study	NC	April	20	8.0	0.8	0.3

^aLocation is assumed to be the Midwest of the USA, but location is not specified in paper.

Table 2. It can be observed that the H₂S fluxes from this study are similar to those reported by the Blunden and Aneja¹⁶ study, which made measurements at the same sampling site as this study. Both studies have their highest fluxes in the summer and their lowest in the winter. For the fall sampling season, the flux is higher in this study than in comparison to Blunden and Aneja.¹⁶ Conversely in the spring season, Blunden and Aneja¹⁶ reported flux is slightly higher. In comparison to other swine CAFO studies in the U.S., the fluxes are generally 2–3 orders of magnitude lower. A possible reason for higher fluxes in the previous studies is related to lagoon sulfide content. Zahn et al.¹⁴ lagoon sulfide concentrations are considerably higher than those reported by Blunden and Aneja,¹⁶ and approximately an order of magnitude higher than those reported in this study. Therefore, the higher lagoon sulfide content may account for the differences in fluxes between the studies, however there is no lagoon sulfide concentration reported in Lim et al.¹⁵ study. To confirm this hypothesis, it is suggested that further H₂S lagoon flux measurements are made in conjunction with lagoon sulfide measurements. Furthermore, upon confirmation of this hypothesis, a comprehensive analysis of the factors that result in lower sulfide concentrations in North Carolina is needed, as there may be possible policy implications for the reduction of H₂S emissions.

3.1.2. Diurnal Trends. The diurnal trends of seasonal H₂S emissions are shown in Figure 1a,b. It should be noted that for the diurnal trend analysis and analysis thereafter that H₂S emissions caused by “bubble transport” mechanisms⁴⁰ have been omitted. In the summer season (Figure 1a), it can be observed that the fluxes are lowest during the afternoon and evening with a minimum of 1.53 μg m⁻² min⁻¹ at 18:00. During the night and morning hours the fluxes generally increase, peaking at 10:00 with a value of 4.21 μg m⁻² min⁻¹. The fall diurnal flux trend (Figure 1a) is similar to the summer season, with fluxes lowest in the afternoon and evening (minimum of 0.58 μg m⁻² min⁻¹ at 21:00) before increasing during the night and morning. The highest peak occurs at 6:00 with a value of 1.11 μg m⁻² min⁻¹. For winter and spring, the diurnal trends are not as clear (Figure 1b). This is likely the result of the small diurnal variation of winter and spring hourly fluxes, with fluxes ranging from 0.04 to 0.11 μg m⁻² min⁻¹ and 0.05–0.13 μg m⁻² min⁻¹, respectively. However, generally, the winter fluxes are highest during the afternoon and evening and the spring fluxes are highest during the daytime hours.

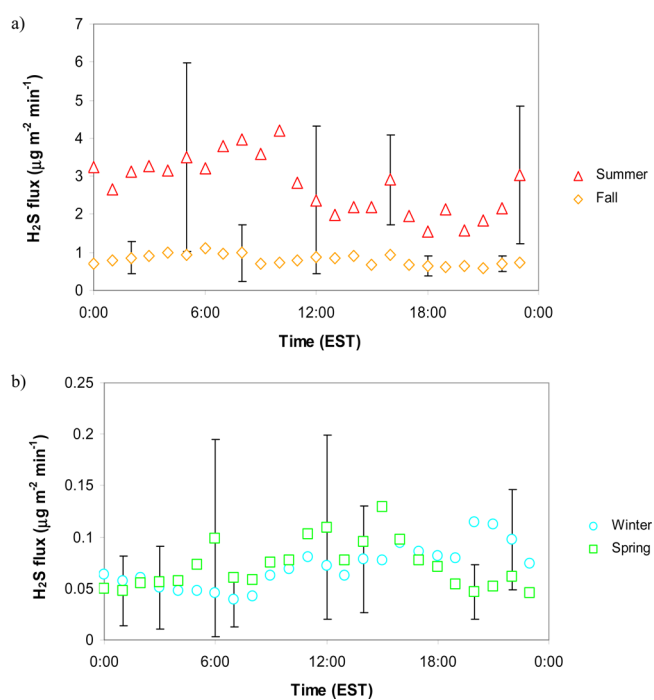


Figure 1. The composite hourly average diurnal trend of H₂S flux (μg m⁻² min⁻¹) for (a) the summer and fall sampling season, (b) the winter and spring sampling season. Error bars represent ±1 standard deviation and are randomly selected.

3.1.3. The Influence of Environmental Parameters on H₂S Lagoon Flux. The relationships between H₂S lagoon flux trends and individual environmental parameter trends were investigated by using linear regression. Wind speed was not included in statistical analysis as the chamber does not simulate the diurnal pattern of wind speed. Lagoon sulfide concentration was also excluded from statistical analysis due to a limited data set. The results of this analysis are provided in figures in the SI. This analysis found that lagoon pH, lagoon temperature, and air temperature all had a significant (*p*-value < 0.01) relationship with H₂S lagoon flux. Lagoon pH had a negative relationship with H₂S lagoon flux, whereas lagoon temperature and air temperature had positive relationships with H₂S lagoon flux. Multiple linear regression analysis was performed to confirm the influence of environmental parameters on H₂S flux and to develop a statistical observational model.

Statistical analysis was performed using SAS (Statistical analysis software v8, Cary, NC). As mentioned, H₂S data was collected continuously as 15 min averages, therefore each data point is not necessarily independent of another. As a result, when performing multiple linear regression, autocorrelation was taken into account. Therefore, the H₂S statistical observational model was determined using autoregression and Yule-Walker estimates. Parameters were deemed significant if their *p*-value was <0.05. Using this statistical technique, the best-fitting model was the following:

$$\begin{aligned} \text{Log H}_2\text{S flux} = & 4.5003 - 0.7573(\text{pH}) + 0.0262(L_T) \\ & + 0.0202(A_T) \end{aligned} \quad (14)$$

where log H₂S flux is in units of $\mu\text{g m}^{-2} \text{min}^{-1}$, pH is unitless, L_T is the lagoon temperature in °C and A_T is the air temperature in °C. The statistical observation model had an r^2 value of 0.68 ($p < 0.01$). In this model, pH ($p < 0.01$) is the most dominant environmental parameter, increasing H₂S lagoon emissions as it decreases. This relationship was expected as in the pH range of 7–8.5 (typical pH of anaerobic hog lagoon), the fraction of H₂S available decreases as pH increases (see figure in the SI). Lagoon temperature ($p < 0.01$) had the second largest influence on H₂S flux, increasing H₂S lagoon fluxes as it increases. However, this influence was a lot weaker than that of pH. The relationship between lagoon temperature and H₂S flux occurs as an increase in lagoon temperature, increases the diffusivity of the solute and lowers its solubility resulting in an increase in the overall mass transfer coefficient,⁴¹ thus increasing H₂S fluxes. Ambient air temperature ($p < 0.01$) has the smallest influence of the environmental parameters. Similarly to lagoon temperature, H₂S emissions increased as air temperature increased. A proposed explanation for this is related to the influence of air temperature and lagoon temperature on near-surface atmospheric stability,^{42,43} and thus the overall mass transfer coefficient. During times when air temperature is less than the lagoon temperature the conditions would be unstable at the air-surface interface, resulting in enhanced turbulence and thus increasing the mass transfer rate and therefore fluxes. For ~80% of the data collected in this study, the air temperature was less than the lagoon temperature, therefore this explanation supports the observed relationship in eq 14 between air temperature and H₂S flux.

3.2. Modeling of H₂S Manure Emissions. **3.2.1. Evaluation of Air-Manure Interface Mass Transfer Model.** The A-MI mass transfer model was evaluated by substituting hourly averaged measured environmental parameters during lagoon sampling into the model. For lagoon sulfide concentration, the average seasonal value was used for each season. These model predicted H₂S flux values were then compared to the corresponding hourly averaged measured H₂S lagoon flux values. It should be noted that predicted H₂S fluxes could only be modeled, when a full set of measured environmental parameters were available. The relationship between measured and predicted H₂S fluxes were determined using a line of best fit with the intercept set to zero, and is shown in Figure 2. It can be observed that the model performs well in predicting H₂S fluxes with a slope of 1.13 and an r^2 value of 0.60. Further evaluation of the performance of the model was conducted by calculating the mean bias (eq 15), the normalized mean bias (eq 16), the mean error (eq 17), and the normalized mean error (eq 18).

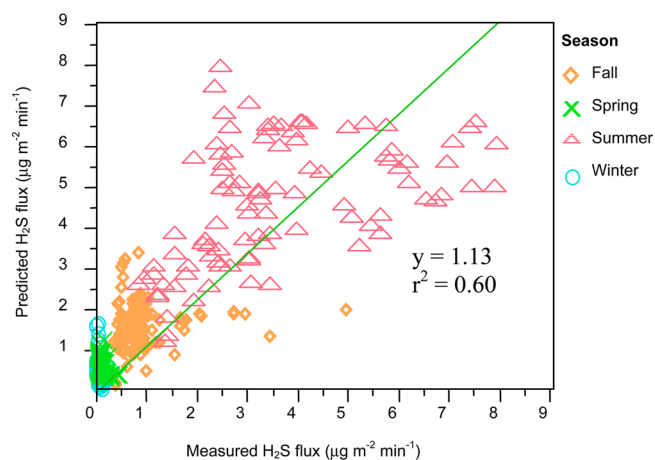


Figure 2. AM-I model predicted hourly H₂S flux vs corresponding measured hourly H₂S flux. Data points ($n = 495$).

$$\frac{1}{N} \sum_{i=1}^N (J_{\text{mod}}(i) - J_{\text{meas}}(i)) \quad (15)$$

$$\frac{\sum_{i=1}^N J_{\text{mod}}(i) - J_{\text{meas}}(i)}{\sum_{i=1}^N J_{\text{meas}}(i)} \times 100\% \quad (16)$$

$$\frac{1}{N} \sum_{i=1}^N |J_{\text{mod}}(i) - J_{\text{meas}}(i)| \quad (17)$$

$$\frac{\sum_{i=1}^N |J_{\text{mod}}(i) - J_{\text{meas}}(i)|}{\sum_{i=1}^N J_{\text{meas}}(i)} \times 100\% \quad (18)$$

where N is the number of data points, J_{mod} and J_{meas} are the corresponding model predicted and measured flux values and i the i th model-measurements data points. The model was found to overpredict measured fluxes with a mean bias value of $0.655 \mu\text{g m}^{-2} \text{min}^{-1}$, and a normalized mean bias value of 67.0%. The mean error and normalized mean error values were $0.811 \mu\text{g m}^{-2} \text{min}^{-1}$ and 82.9%, respectively. The average predicted seasonal fluxes were slightly higher than their corresponding measured seasonal fluxes, with predicted flux values of $4.65 \mu\text{g m}^{-2} \text{min}^{-1}$ for summer, $1.65 \mu\text{g m}^{-2} \text{min}^{-1}$ for fall, $0.52 \mu\text{g m}^{-2} \text{min}^{-1}$ for winter, and $0.58 \mu\text{g m}^{-2} \text{min}^{-1}$ for spring.

One possible reason for the overprediction in model fluxes may be related to the measured lagoon sulfide concentrations. As mentioned, two-thirds of sulfide concentrations were below the detection limit of 1 mg L^{-1} , and therefore these samples were assigned a half detection limit value (0.5 mg L^{-1}). It is possible that the majority of these samples had a sulfide concentration lower than this. In this case, the average seasonal sulfide concentration would be lower, resulting in lower predicted fluxes. Furthermore, the over prediction may be the result of using a pH value measured at a lagoon depth of ~7 cm. Blanes-Vidal et al.¹⁸ developed a pH buffer model. The pH buffer model is based on the theory that surface pH (i.e., at a depth of 1 mm) is different from the pH centimeters below the surface due to the volatilization of gases from the surface manure. The results of the pH buffer model indicate that for anaerobic lagoons, surface pH could increase by ~0.6 if the waste is “undisturbed” (i.e., no mixing). As discussed, an increase in pH would decrease the amount of H₂S available in the waste. Therefore, it may be that pH values used for

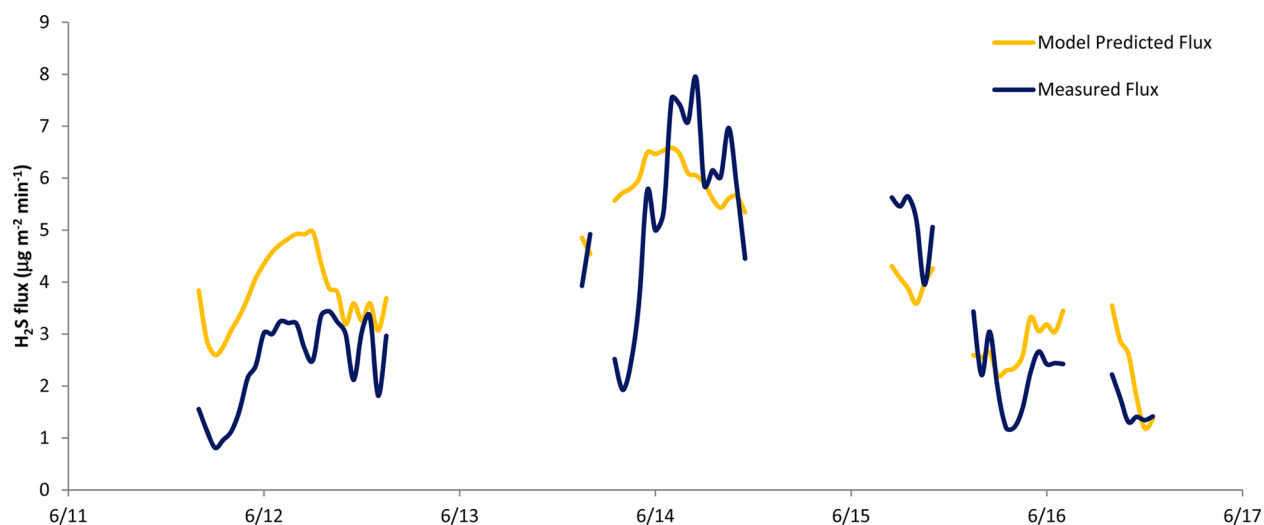


Figure 3. A-MI mass transfer model predicted and measured hourly H_2S flux during the summer sampling season from June 11th to June 16th.

predicting fluxes in this study, which was measured at a depth of ~ 7 cm were lower than the surface pH, which could explain the over prediction of fluxes by the model.

The model also performed fairly well in predicting the influence of environmental parameters on lagoon flux for the summer and fall seasons. Figure 3 presents the measured and model predicted hourly flux values in the summer season from June 11th to June 16th. It can be observed that in addition to having a similar magnitude of predicted flux, the model predicted flux values vary in a pattern similar to the measured flux values. The model fluxes were not as accurate in predicting winter and spring flux variations. However, the performance of the model was difficult to evaluate for the winter and spring seasons due to the low fluxes and thus the small variation in flux during these sampling periods.

To assess the effect of environmental parameters on the A-MI mass transfer model predicted flux values, a sensitivity analysis was performed. A description of the sensitivity analysis and the accompanying results are provided in the SI.

3.2.2. Model Application and Uncertainties. As a result of the methodology used in developing the A-MI model, the model could be applied to predict H_2S CAFO emissions from different manure types, and in different environmental, production, and management conditions. However, it is important to consider uncertainties associated with the model. Of the three main components of the A-MI mass transfer model (the dissociation constant, the Henry's law constant, and the overall mass transfer coefficient), the greatest modeling uncertainty is likely in the development of the overall mass transfer coefficient as both the dissociation constant and the Henry's Law constant are modified for the properties of North Carolina anaerobic lagoon waste. As previously described (section 2.2.1.), in comparison to studies that have been previously used for developing the H_2S mass transfer coefficient, the Santos et al.²⁰ study has a number of advantages, however, there are still some uncertainties associated with using this study. In the Santos et al.²⁰ study, the data set was not empirically developed in conditions where the air temperature was less than the liquid temperature. In addition, it would be useful to develop an overall mass transfer coefficient in a greater range of environmental conditions. Furthermore, a more accurate empirical overall mass transfer coefficient could be developed, if while varying an individual environmental

parameter, the other environmental parameters were kept constant during the experiments. From this, a new expression for the overall mass transfer coefficient could be developed using dimensional analysis. There is also uncertainty associated with the mass transfer coefficient correction value (0.6) used in this study, which was based on an empirical study by Yongsiri et al.,³⁵ where the H_2S overall mass transfer coefficient in wastewater was determined to be 40% less than in deionized water. The Yongsiri et al.³⁵ study was conducting using municipal sewerage wastewater, therefore it is unknown how representative this value is for different types of animal waste.

A further uncertainty associated with the use of the overall mass transfer coefficient developed in the Santos et al.²⁰ study is that it does not consider chemical reactions in the manure. When taking into account chemical reactions, the concentration at the gas-liquid interface is calculated using the diffusivity of the compounds involved in the chemical reactions. However, as previously mentioned, there are no known empirical experiments available which have determined the diffusivity of H_2S and HS^- in animal waste. Therefore, the only available values in literature are for the diffusivity of H_2S and HS^- in water. Using these values will likely lead to errors in calculating the liquid mass transfer coefficient and thus a compounds concentrations at the liquid interface.

■ ASSOCIATED CONTENT

📄 Supporting Information

Lagoon and spray technology waste management method; dynamic flow-through chamber and H_2S lagoon flux measurements; 450C $\text{H}_2\text{S}/\text{SO}_2$ analyzer; explanations for the influence of environmental parameters on the overall mass transfer coefficient; sensitivity analysis of air-manure interface mass transfer model; additional tables, figures, and references. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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