



Modeling hydrogen sulfide emissions across the gas–liquid interface of an anaerobic swine waste treatment storage system

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ABSTRACT

Hydrogen sulfide (H₂S) is a colorless gas emitted during decomposition of hog manure that produces an offensive “rotten egg” smell and is considered a toxic manure gas. In the southeastern United States, anaerobic waste treatment lagoons are widely used to store and treat hog excreta at commercial hog farms. Hydrogen sulfide is produced as manure decomposes anaerobically, resulting from the mineralization of organic sulfur compounds as well as the reduction of oxidized inorganic sulfur compounds by sulfur-reducing bacteria. The process of H₂S emissions from anaerobic waste treatment lagoons are investigated utilizing a two-film model with three different modeling approaches: Coupled Mass Transfer with Chemical Reactions Model with the assumption (1) pH remains constant in the liquid film (MTCR Model I) and (2) pH may change throughout the liquid film due to diffusion processes that occur within the film (MTCR Model II); and (3) a Mass Transfer Model which neglects chemical reactions (MTNCR Model) in the gas and liquid films.

Results of model predictions are consistent with previous works, which show that flux is largely dependent on the physicochemical lagoon properties including sulfide concentration, pH, and lagoon temperature. Air temperature and low wind velocities (e.g., <3.25 m s⁻¹) have negligible impact on flux. Results also indicate that flux values decrease with increased film thickness. The flux was primarily influenced by variations in the liquid film thickness, signifying that the H₂S flux is driven by liquid-phase parameters. Model results were compared with H₂S flux measurements made at a swine waste treatment storage lagoon in North Carolina using a dynamic emission flux chamber system in order to evaluate model accuracy in calculating lagoon H₂S emissions. The MTCR Model II predicted the highest increase in emission rates as aqueous sulfide concentration was increased. The MTNCR Model showed the highest dependence on pH. All three models showed good agreement in diurnal comparison with flux measurements; however, each model significantly over predicted the measured flux rates. The MTNCR Model estimates were closest to experimental values, predicting 3–35 times the actual measured values.

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1. Introduction

Hydrogen sulfide (H₂S) is a colorless, potentially harmful gas released from swine manure (US EPA, 2001a). It is produced as manure decomposes anaerobically, resulting from the mineralization of organic sulfur compounds as well as the reduction of oxidized inorganic

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sulfur compounds such as sulfate by sulfur-reducing bacteria (US EPA, 2001a). With a low odor threshold ranging from 0.0005 to 0.3 ppm (ATSDR, 2004), it is also one of the primary gases released from swine facilities that is associated with odor complaints due to its characteristic “rotten egg” smell.

Over the last few years, changes in livestock production methods in the US have led to the emergence of large-scale commercial livestock operations, substantially increasing the number of animals in geographically concentrated areas (Aneja et al., 2006). As emissions of trace gases (i.e., nitrogen and sulfur species) likely increase in parallel with the growth and consolidation of this industry, it is important to ensure that these operations do not exceed state regulatory levels for gases such as H₂S.

To date, few studies have reported H₂S emissions from waste storage treatment lagoons (Zahn et al., 2002; Lim et al., 2003; Blunden and Aneja, 2008). Arogo et al. (2000) studied the concentration and production of H₂S from stored liquid hog waste in a laboratory experiment. Arogo et al. (1999) have investigated the effects of environmental parameters (wind speed and air temperature) and manure properties (solids content and liquid temperature) in the laboratory and developed an overall mass transfer coefficient for emission of H₂S from liquid swine manure. The US Environmental Protection Agency (EPA) has developed a comprehensive model, WATER9, Version 2.0 (US EPA, 2001b) for estimating emissions of individual waste constituents in wastewater collection, storage, treatment, and disposal facilities.

In this study, a two-layer model of gas–liquid interchange for exchange between air and water is used to predict H₂S flux across an air–water interface. The interface between the two layers is often considered a two-layer film system (Whitman, 1923; Danckwerts, 1970; Liss and Slater, 1974). The two-film layer consists of well-mixed gas and liquid films adjacent to the interface. The rate of transfer is controlled by molecular diffusion through the stagnant boundary layer.

Similar models have been developed to predict emissions of ammonia (Aneja et al., 2001), dimethyl sulfide (Aneja and Overton, 1990), sulfur dioxide, nitrogen oxide, methane, carbon monoxide (Liss and Slater, 1974), and carbon dioxide (Quinn and Otto, 1971). It is noted that other modeling approaches may be utilized to predict gas exchange at the air–liquid interface (e.g., Danckwerts, 1970).

For comparison, three process-based models have been developed in order to predict the rates of H₂S flux from swine waste storage and treatment lagoons based on different conditions in the gas and liquid films. Two coupled Mass Transfer and Chemical Reactions Models based on the concept of simultaneous mass transfer and equilibrium chemical reaction were developed. One model considers flux based on the assumption of constant pH throughout the liquid film (MTCR Model I) and a second model considers a possible pH gradient in the liquid film due to diffusion processes (MTCR Model II). A third mass transfer model considers the hydrogen sulfide concentration in the bulk gas and liquid phases, neglecting chemical reactions in the gas and liquid films (MTNCR Model). Field

experiments to measure H₂S emissions from an anaerobic waste treatment lagoon were previously conducted at a commercial swine finishing operation in North Carolina over each of the four predominant seasons (Blunden and Aneja, 2008). These experimental results are used to evaluate the model's accuracy in calculating lagoon H₂S emissions.

2. Field experimental methods and model calculation

2.1. Experimental flux measurements

Hydrogen sulfide flux measurements were made at a commercial swine finishing operation in eastern North Carolina (Blunden and Aneja, 2008). Waste from the eight on-site animal confinement houses were flushed out with recycled lagoon effluent and discharged into the anaerobic lagoon from each house approximately once per week (varying days for each house).

Hydrogen sulfide flux was measured using a dynamic flow through chamber system (Aneja et al., 2000), consisting of a fluorinated ethylene propylene (FEP) Teflon-lined open bottom cylinder inserted into a floating platform. When the platform and chamber system were placed at a randomly chosen location on the lagoon, the chamber penetrated the lagoon surface to a depth of 6–7 cm, thus forming a seal between the lagoon surface and the air inside the chamber. Compressed zero-grade air was pumped through the chamber at a known flow rate and the air inside the chamber was continuously stirred by a motor driven Teflon impeller. Once the chamber reached steady-state conditions, samples were drawn through Teflon tubes to a Thermo Environmental Instruments (TEI) Model 450C pulsed fluorescence H₂S/SO₂ analyzer where the volumetric concentration was measured.

Continuous measurements were made for about a 1-week period during four seasons, beginning October 2004 and ending June 2005, in order to determine seasonal trends. A Model CSIM11 pH probe and a CS107 temperature probe (Campbell Scientific Inc., Logan, UT) were submerged in the lagoon at a depth of ~6–7 cm beneath the surface in order to continuously monitor near-surface lagoon pH and lagoon temperatures. The measured pH is considered to be part of the bulk liquid phase, which is defined as the well-mixed region of the liquid (lagoon).

To determine the concentration of total sulfide samples in the slurry, liquid samples were collected from the lagoon surface 1–2 times per day (usually between 10:00 and 14:00 h) during the flux experiment and were preserved with 6 N sodium hydroxide and 2 N zinc acetate to pH > 9, according to North Carolina Division of Water Quality (NC DWQ) specifications. NC DWQ performed colorimetric analyses, Standard Method 4500-S-2-D (Greenberg et al., 1999), to determine sulfide content.

2.2. Mass transport model

The principal characteristic of this transport model is the two-layer film model of molecular exchange of gases

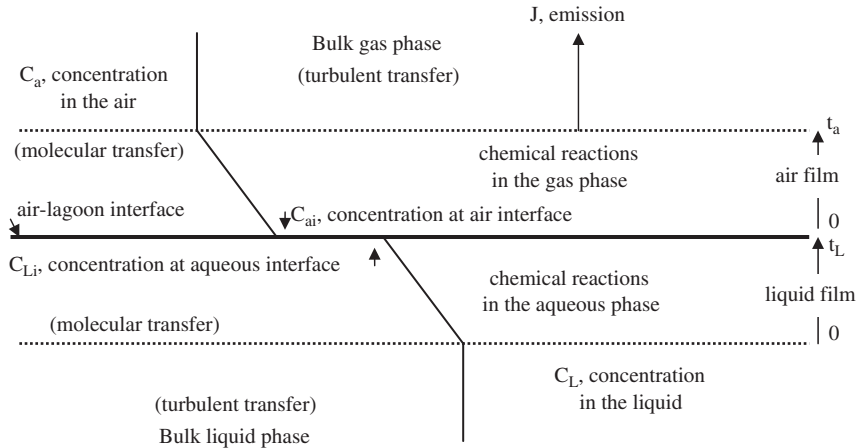
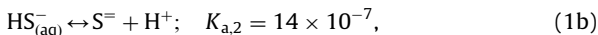
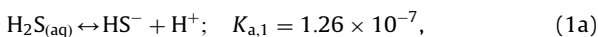


Fig. 1. Two-film theory of mass transfer for the exchange of gases across the gas-liquid system.

between water and air (Whitman, 1923; Danckwerts, 1970; Liss and Slater, 1974). Fig. 1 shows a schematic of the two-film concept. Each layer is a laminar surface layer of thickness, t_i ($t_i = t_L$ and t_a for liquid and air phase thickness, respectively), extending from the air-liquid interface to a well-mixed region in the interior of the liquid (lagoon) and the air (atmosphere). All resistance to mass transport across the interface is due to the layer in which transport occurs by molecular processes.

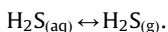
2.2.1. Mass transport model with chemical reactions (MTCR)

These models explicitly take into account molecular diffusion and chemical reactions. In the liquid film, only hydrogen sulfide's reversible reaction in water is considered. In this film, molecular H_2S exists in equilibrium with the bisulfide ion (HS^-) and the sulfide anion ($S^{=}$). All three comprise total sulfide and are related by the following equilibrium equations:

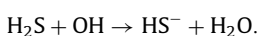


where $K_{a,1}$ and $K_{a,2}$ are the rate dissociation constants for the above equations. As pH shifts from alkaline to acidic ($pH < 7$) the potential for H_2S emissions increases. The sulfide anion can form at $pH > 12$ (Snoeyink and Jenkins, 1980), well above the range for a typical hog lagoon, and therefore is not considered for this modeling exercise. It is important to note that only the molecular $H_2S_{(aq)}$ fraction, not the ionized forms (HS^- and $S^{=}$), can transfer across the gas-liquid interface (US EPA, 1974).

For the physicochemical process of H_2S transfer across the gas-liquid interface, the transfer from the aqueous phase $H_2S_{(aq)}$ into the gaseous phase $H_2S_{(g)}$ may be expressed by



In the gas phase, hydrogen sulfide is known to react solely with the hydroxyl radical $[OH]$ (Seinfeld and Pandis, 1998):



In the gas film, $[OH]$ is assumed to have a constant concentration, giving an effective first-order reaction for hydrogen sulfide, with first-order reaction rate constant of H_2S in the gas phase, k_{ra} , provided as

$$k_{ra} = k[OH], \quad (2)$$

where k is the temperature dependent rate coefficient for this reaction.

The following equation describes the transport of hydrogen sulfide in the gas phase:

$$D_a \left(\frac{d^2[H_2S(z)]}{dz^2} \right) = k_{ra} \times [H_2S](z), \quad (3)$$

where $[H_2S](z)$ is the hydrogen sulfide concentration at the height of z in a gas film of thickness t_a and D_a is the molecular diffusion of hydrogen sulfide in the gas phase. The boundary conditions are

$$z = 0; \quad [H_2S](0) = [H_2S]_{ai}, \quad (4)$$

$$z = t_a; \quad (t_a) = [H_2S]_a, \quad (5)$$

where $[H_2S]_{ai}$ and $[H_2S]_a$ are the concentrations of hydrogen sulfide at the interface and in the well-mixed bulk of the gas phase. The solution to the mass transport equation results in hydrogen sulfide flux to the atmosphere being expressed in terms of film thickness, gas-phase hydrogen sulfide diffusion coefficient, the effective first order rate constant, and the concentrations at the film boundaries.

2.2.1.1. MTCR Model I: pH constant throughout liquid film.

For this model, MTCR Model I, pH is assumed constant in the liquid film. Based on this assumption, indicating single-reactant single-product, a theoretical result of Olander (1960) is used to define the hydrogen sulfide flux, J_{i1} , in the liquid phase at the air-liquid interface:

$$J_{i1} = \left(\frac{D_L}{t_L} \right) ([H_2S]_L - [H_2S]_{Li}) \left(1 + \frac{D_{HS^-}}{D_L} K_{rL} \right), \quad (6)$$

where D_{HS^-} and D_{L} are the diffusivities of hydrogen sulfide anion and hydrogen sulfide in the liquid phase, respectively; t_{L} is the thickness of the liquid film. Hydrogen sulfide concentrations at the interface and in the well-mixed bulk of the liquid phase are given by $[\text{H}_2\text{S}]_{\text{Li}}$ and $[\text{H}_2\text{S}]_{\text{L}}$, respectively. K_{rL} is the overall effective equilibrium constant and is given by $K_{\text{rL}} = K_{\text{L}}/\text{H}^+$ in which K_{L} (same as $K_{\text{a,1}}$) is the dissociation constant for the reaction of hydrogen sulfide in the water.

Assuming the gas-phase and liquid-phase hydrogen sulfide concentrations at the air–liquid interface and are related by Henry's Law constant (H), Eq. (6) can be combined with a gas-phase interfacial expression for flux based on the solution to Eq. (3). The result is an expression for the flux of hydrogen sulfide from the lagoon water to the atmosphere under the assumption that pH remains constant throughout the liquid film.

2.2.1.2. MTCR Model II: pH gradient in liquid film. For this model, MTCR Model II, pH varies in the liquid film. Based on the work previously done by Olander (1960) to predict the effect of various types of infinitely rapid equilibrium chemical reactions on the liquid-phase mass transfer coefficient, we have developed a flux equation that considers the equilibrium chemical reaction for dissociation of a single molecular substance into its ionized forms (i.e., dissociation of hydrogen sulfide). As opposed to single-reactant single-product, this non-linear model considers the possible gradient change in pH from the bulk liquid phase to the gas–liquid film interface due to molecular diffusion and transport processes of all associated species (H_2S , HS^- , H^+). Details for this model development are provided in Blunden (2006). It should be noted that H_2S is one component of a complex matrix of gases and organics in liquid manure, which will also contribute to the pH of the system based on their concentration levels.

The hydrogen sulfide flux, J_{i2} , in the liquid phase at the air–liquid interface is determined by

$$J_{\text{i2}} = \frac{1}{2t_{\text{L}}} \left(\frac{2D_{\text{L}}[\text{H}_2\text{S}]_{\text{L}} - 2D_{\text{H}_2\text{S}}[\text{H}_2\text{S}]_{\text{Li}} + 2D_{\text{HS}^-}[\text{HS}^-]_{\text{L}}}{-\beta + \sqrt{\beta^2 + 4D_{\text{HS}^-}D_{\text{H}^+}K_{\text{L}}[\text{H}_2\text{S}]_{\text{Li}}}} \right), \quad (7)$$

where $[\text{HS}^-]_{\text{L}}$ denotes bisulfide ion in the bulk liquid region; D_{L} , D_{HS^-} , and D_{H^+} are the diffusivities of molecular hydrogen sulfide, bisulfide ion, and hydrogen ion, respectively; t_{L} is the thickness of the liquid film. Hydrogen sulfide concentrations at the interface and in the well-mixed bulk of the liquid phase are given by $[\text{H}_2\text{S}]_{\text{Li}}$ and $[\text{H}_2\text{S}]_{\text{L}}$, respectively. K_{L} is the dissociation constant for the equilibrium equation of hydrogen sulfide in the liquid; and β is determined by $D_{\text{HS}^-}[\text{HS}^-]_0 - D_{\text{H}^+}[\text{H}^+]_0$, where $[\text{HS}^-]_0$ and $[\text{H}^+]_0$ are the concentrations of bisulfide ion and hydrogen ion at any point in the liquid film. As stated previously, only molecular hydrogen sulfide, not the ionic species, can cross the gas–liquid interface.

Given the same equilibrium assumptions as MTCR Model I, Eq. (7) can be combined with a gas-phase interfacial expression for flux based on the solution to Eq. (3). The result is an expression for the flux of

hydrogen sulfide from the lagoon water to the atmosphere under the assumption that a pH gradient exists in the liquid film.

2.2.2. Mass transport model neglecting chemical reactions (MTNCR)

Without chemical reactions considered in the gas and liquid films, and assuming that the turbulent air and liquid regions are well mixed, the hydrogen sulfide flux, J_3 , to the atmosphere may be determined by

$$J_3 = -K(C_{\text{a}} - HC_{\text{L}}), \quad (8)$$

where hydrogen sulfide concentration in the turbulent gas and liquid regions are given by C_{a} and C_{L} , respectively, and K is the overall mass transfer coefficient, which can be expressed by (Whitman, 1923)

$$\frac{1}{K} = \frac{H}{k_{\text{L}}} + \frac{1}{k_{\text{a}}}, \quad (9)$$

where k_{a} and k_{L} are the gas and liquid mass transfer coefficients, respectively, and H is the Henry's Law constant. Wind speed, diffusivity, and kinetic viscosity are parameters used to determine the mass transfer coefficients. For details regarding the calculations used to determine the diffusivities, viscosities, and mass transfer coefficients, and Henry's Law constant for this system, the reader is referred to Blunden (2006).

2.2.3. Mass transfer model parameters

Mass transfer coefficients were obtained from Mackay and Yeun (1983) and Springer et al. (1984) as provided by US EPA (1994) for quiescent wastewater impoundments, and applied to all three models. Due to possible variations in viscosity and diffusion processes, it is reasonable to assume that the liquid mass transfer coefficient for liquid hog waste may be lower than water. Mackay and Yeun (1983) report that their results suggest that mass transfer coefficients will generally be lower in field experiments as opposed to those measured in the laboratory. Yongsiri et al. (2004a) observed a 40% reduction for the liquid mass transfer coefficient of hydrogen sulfide in sewage networks. Based on the results of this study, a "correction factor" of 0.6 was applied to the liquid mass transfer coefficient equations for all model calculations to predict emissions from liquid hog waste. Schwarzenbach et al. (2003) illustrate the generic relationship between the equilibrium air–water partition constant (the non-dimensional Henry's Law constant) as it is related to the Henry's Law constant and temperature. Henry's Law constant values used this model were obtained from Metcalf and Eddy (1979), who report values for hydrogen sulfide as a function of temperature from 0 to 60 °C. Al-Haddad et al. (1989) experimentally evaluated Henry's Law constant of H_2S from 20 to 40 °C both in distilled water and in sewage water from treatment plants. Results from the distilled water correlated well with previous studies (Metcalf and Eddy, 1979; US EPA, 1974), and it was reported that the more complex chemical composition did not appear to influence Henry's Law constant.

3. Results and discussion

3.1. Sensitivity analysis

The three modeling approaches provide flux dependence for hydrogen sulfide emissions on lagoon temperature, lagoon pH, and aqueous sulfide content in the lagoon as well as atmospheric environmental factors such as ambient air temperature, wind speed, and the concentration of H_2S in the ambient air. Practical ranges of these parameters have been considered for the sensitivity analysis. The effect of each parameter was examined by varying the values of the parameter throughout a given range while holding every other parameter value constant. The constant values were obtained from annual average values that were observed at an experimental swine lagoon site in eastern North Carolina and given as follows: sulfide concentration (2 mg L^{-1}), lagoon pH (8.1), lagoon temperature (19°C), air temperature (16°C), wind speed (1.3 m s^{-1}), and ambient H_2S concentration ($10 \mu\text{g m}^{-3}$). It is noted that the measured pH range at the swine lagoon was much smaller (7.9–8.2) than the range of this sensitivity analysis; however, higher and lower values might be typical at other swine lagoons. Additionally the effect of gas and liquid film thicknesses were examined under various temperatures at the lowest, highest, and middle (high+low/2) predicted values during sensitivity analysis on all other parameters. The liquid film thickness

was held constant at the middle value, 0.047 cm , as the gas film thickness was varied and the gas film thickness was held constant at the middle value, 0.912 cm , as the liquid film was varied.

3.1.1. Effect of lagoon parameters on hydrogen sulfide flux

Although the flux estimations vary greatly between models, there is agreement for all models, indicating a decrease in emissions as lagoon temperatures are increased (Fig. 2a). Since diffusivity and viscosity generally increase as temperature increases, this finding may be appear to be counterintuitive. However, as the dissociation constant increases the H_2S dissociation also increases (US EPA, 1974; Yongsiri et al., 2004b) and therefore less molecular H_2S is available for transfer across the gas-liquid interface. The effect of temperature on the amount of hydrogen sulfide present in the liquid overrides the effect of increased temperature on other parameters such as diffusivity and viscosity in the model. For the range of temperatures used in this analysis, the MTCR I and II Models show a decrease in emissions of $\sim 10\%$, and the MTNCR Model predicts a higher rate of flux decrease, $\sim 55\%$.

Lagoon pH controls the chemical equilibrium of the H_2S – HS^- – S^{2-} system in the aqueous phase. All three models indicate a decrease in H_2S flux as pH is increased from 6.5 to 8.5 (Fig. 2b); however, the MTNCR Model has a higher rate of decrease than the MTCR Models although the predicted flux is lower for all pH ranges.

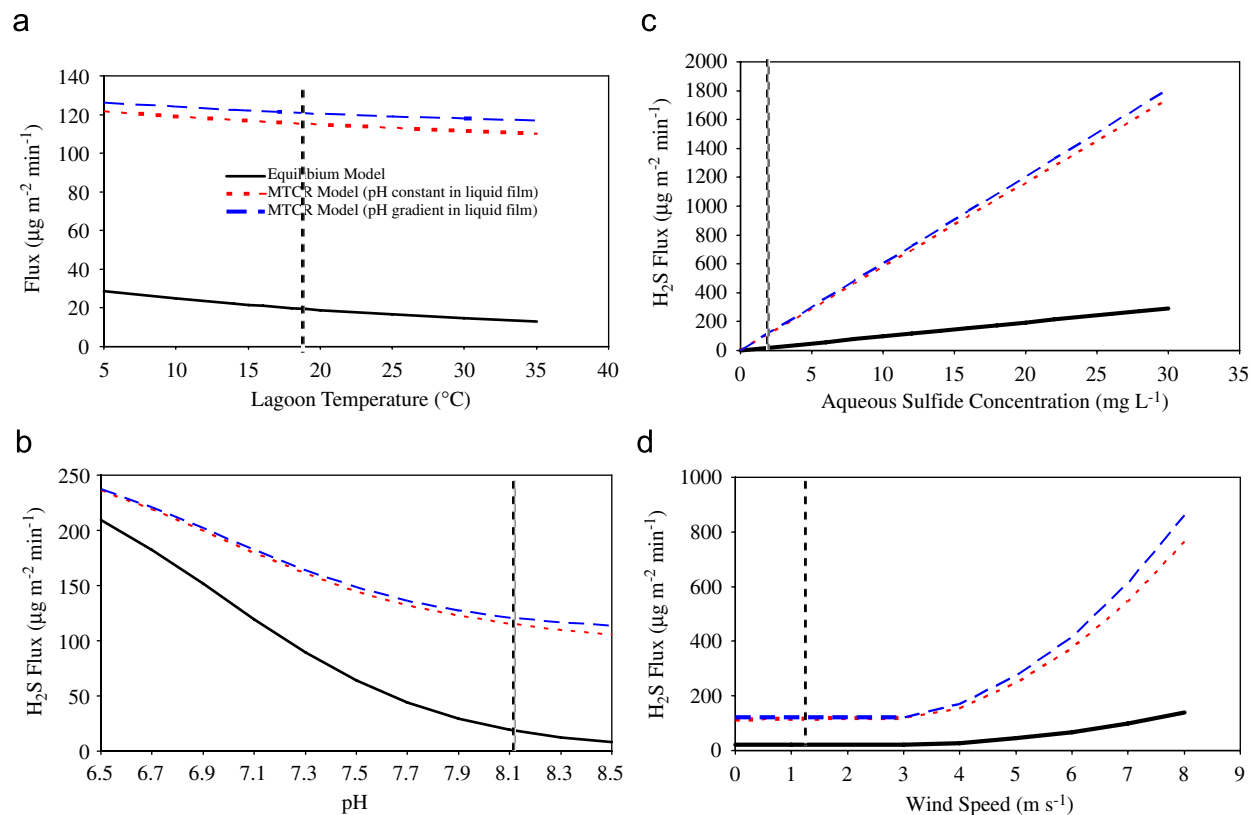


Fig. 2. Sensitivity of hydrogen sulfide emissions with respect to (a) lagoon temperature, (b) lagoon pH, (c) aqueous sulfide concentration, and (d) wind speed measured at 10 m.

A linear increase was observed for all three models as sulfide concentration was increased (Fig. 2c). Predicted emissions for the MTCR Model I and MTCR Model II were ~6 times higher than the MTNCR Model based on the increase in aqueous sulfide. In diluted water H^+ diffuses at more than 6 times the rate of H_2S (Cussler, 1997). Consideration of all gaseous compounds that take part in the equilibrium reaction (H_2S, HS^-, H^+) indicate that the pH decreases toward the top of the liquid film due to higher H^+ diffusion rate, thereby increasing the flux rate at the interface and thus accounting for the slightly higher flux predicted in MTCR Model II compared to Model I.

3.1.2. Effect of atmospheric environmental parameters on hydrogen sulfide flux

Hydrogen sulfide is a relatively insoluble gas and the flux is primarily driven by the resistance in the liquid phase (Lewis and Whitman, 1924; Liss and Slater, 1974; Stumm and Morgan, 1996). The gas mass transfer coefficient (Mackay and Yeun, 1983), which is a function of wind speed, therefore is expected to have little effect on the hydrogen sulfide emissions process. The liquid mass transfer coefficient correlation provided by Springer et al. (1984) is applicable for low wind speeds (reference height 10 m), $<3.25 \text{ m s}^{-1}$, and does not take wind speed into account. Instead, the ratio of diffusivity of hydrogen sulfide to diffusivity of ethyl ether is considered. At higher wind speeds, Mackay and Yeun (1983) empirical equations are applied. These equations consider the effect of friction velocity on the liquid mass transfer coefficient, and indicate exponential increase in H_2S flux as wind velocity is increased at 10 m height. From Fig. 2d, wind speed variation from 3.0 to 8.0 m s^{-1} predicts a flux change

from 19 to $99 \mu\text{g m}^{-2} \text{ min}^{-1}$ for the MTNCR Model, and more dramatic changes for the MTCR I Model, 165 to $836 \mu\text{g m}^{-2} \text{ min}^{-1}$ and the MTCR II Model, from 171 to $884 \mu\text{g m}^{-2} \text{ min}^{-1}$. However, for higher wind velocities (i.e., $>3.25 \text{ m s}^{-1}$) measured in the field experiments, no increase in H_2S emissions was observed (Blunden and Aneja, 2008). In the event that pH is more acidic, windspeed will play a greater role in emissions across the gas–liquid interface. For all three models, change in H_2S flux was negligible as air temperature and ambient air H_2S concentration were increased.

3.1.3. Effect of film thickness on hydrogen sulfide flux

Sensitivity analysis results for variations in film thickness are presented in Table 1. Lower film thicknesses are generally associated with more turbulent conditions (Quinn and Otto, 1971; Liss and Slater, 1974). As the liquid film thickness was increased, emissions for both MTCR models decreased almost linearly. There was negligible change in emissions as the gas film thickness was changed. It is therefore shown that hydrogen sulfide flux is indeed driven primarily by the liquid phase, as indicated in previous works (e.g., Stumm and Morgan, 1996). Hence, the contribution of environmental parameters on the air side (i.e., air temperature and wind speed) may have a small impact on the emission process compared to liquid side parameters such as lagoon temperature and the Henry's Law constant.

3.2. Model results compared with experimental data

In order to examine the diurnal variations of the emission rates predicted emissions were compared to flux

Table 1

Sensitivity of H_2S emissions with respect to air and liquid film thicknesses for each MTCR Model

Lagoon temperature, T_L ($^{\circ}\text{C}$)	Liquid film thickness, t_L (cm)	Air film thickness, t_a (cm)	Henry's Law constant, H (M) _a / (M) _L	MTCR (pH constant) H_2S flux, J ($\mu\text{g m}^{-2} \text{ min}^{-1}$)	MTCR (pH gradient) H_2S flux, J ($\mu\text{g m}^{-2} \text{ min}^{-1}$)
<i>Changing liquid film thickness</i>					
5	0.007	0.912	0.249	548	598
5	0.047	0.912	0.249	88	91
5	0.086	0.912	0.249	48	50
15	0.007	0.912	0.323	682	793
15	0.047	0.912	0.323	115	121
15	0.086	0.912	0.323	64	66
25	0.007	0.912	0.401	802	1019
25	0.047	0.912	0.401	146	155
25	0.086	0.912	0.401	81	85
<i>Changing air film thickness</i>					
5	0.047	0.117	0.249	89	91
5	0.047	0.912	0.249	88	91
5	0.047	1.708	0.249	87	91
15	0.047	0.117	0.323	118	121
15	0.047	0.912	0.323	115	121
15	0.047	1.708	0.323	113	120
25	0.047	0.117	0.401	151	156
25	0.047	0.912	0.401	146	155
25	0.047	1.708	0.401	141	155

The following model parameters were held constant: air temperature (19°C), pH (8), wind speed (1.3 m s^{-1}), ambient H_2S concentration ($10 \mu\text{g m}^{-3}$).

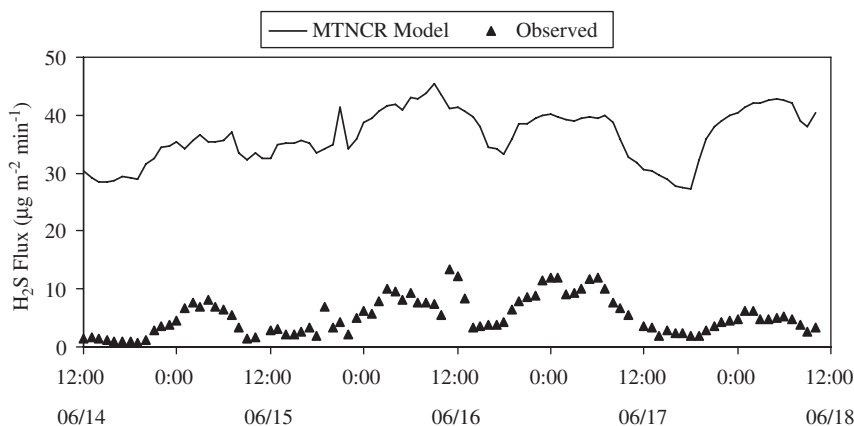


Fig. 3. Comparison of MTNCR Model flux predictions and dynamic flux chamber results for the summer experimental period (14–18 June 2005).

values measured during the summer experimental period. Fig. 3 provides hourly averaged H_2S flux from 14–18 June 2005 plotted against the predicted flux values by the MTNCR Model. There is good qualitative agreement of the diurnal variations of the measured and modeled flux values, both indicating generally increasing emissions during the cooler nighttime hours and a decrease in the daytime as temperatures rise. The model also closely followed the measured emission trend as pH increased or decreased. However, the MTNCR Model predicts emissions ~ 3 – 35 times higher than the measured values. The MTCR I and MTCR II Models (not graphed) both predict the same diurnal trend, however the variation in emissions is much lower and the emission rate are ~ 20 – 125 times higher than measured experimental values for both models. The hourly averaged measured and modeled flux data for all three models for 17 June 2005, along with measured lagoon and environmental parameters are provided in Table 2.

Table 3 shows the average measured H_2S flux values for each season, the measured lagoon and environmental parameters (average and range), and the modeled predicted values. Similar to the summer comparison, each model predicts significantly higher flux than the actual measured values.

As shown during sensitivity analyses and model comparison with measured flux values, both MTCR models predict H_2S flux ~ 5 – 6 times higher than the MTNCR model.

The MTCR models consider chemical reactions and therefore the difference is likely due to one or more of these parameters: diffusion coefficients for H_2S and HS^- , the rate reaction constant for H_2S with the hydroxyl radical in the atmosphere, and the H_2S rate dissociation constant. Uncertainties with these parameters are discussed in further detail in the following section.

3.3. Modeling uncertainties

As shown in Section 3.2, each model showed good agreement in diurnal variation but predicted a significantly higher H_2S flux than was measured in the field

experiments. There are several uncertainties associated with these models that need to be considered. Liquid hog waste is a complex matrix consisting of dozens of aqueous gases, volatile solids, bacteria, etc. It would be expected that factors such as gas and liquid diffusivities, dissociation constants, and liquid mass transfer coefficients would be different than measurements reported from laboratory experiments with clean water; however, the extent is largely unknown. Additionally, the complex matrix of gases and organics will affect the pH of the system. It is difficult to quantify with certainty the effect that pH alone may have on the system.

Regarding the aqueous equilibrium chemistry, the MTCR models consider the diffusivity of the bisulfide ion (HS^-) in the flux calculations. The value used in the model was obtained from Dinus and Redding (1972), who conducted laboratory experiments to determine the diffusivities of H_2S , HS^- , and $S^{=}$. The reported values for H_2S were about two orders of magnitude lower than commonly accepted values and the authors could not explain the discrepancy. Furthermore, after extensive research, no other reported measured values of HS^- diffusion coefficients were found in the literature. It is possible that this may be an inappropriate value, which would significantly alter the H_2S flux prediction. For example, at pH 8.1, by reducing the diffusion coefficient by a factor of two, the flux is reduced by $\sim 58\%$ for both MTCR models. Reducing the diffusion coefficient by a factor of 10 will produce a reduction in flux of 80% and 75%, for MTCR Models I and II, respectively. In previous studies, for the diffusion coefficient of dissolved oxygen, Lin et al. (1998) reported a 45% reduction measured in industrial wastewater, Wise and Houghton (1969) observed a 55% reduction in water containing 20% human red blood cells, and Altman and Dittmer (1971) reported a 67% reduction in water containing 33% methemoglobin. Based on these observations it is reasonable to assume that the diffusion coefficients for HS^- as well as H_2S and H^+ may be significantly reduced in liquid swine waste.

It is also possible that the rate dissociation constant for H_2S in water may differ in liquid waste. Arago et al. (2003) conducted a laboratory experiment for dissociation constant of ammonium ion in deionized water and anaerobic

Table 2

Modeled flux values for the data collected on 17 June 2005 during the summer experimental period

Time	Sulfide (mg L ⁻¹)	Lagoon temperature (°C)	pH	Wind speed (m s ⁻¹)	Air temperature (2 m) (°C)	Measured (μg m ⁻² min ⁻¹)	Modeled results		
							Equilibrium (μg m ⁻² min ⁻¹)	MTCR (pH constant) (μg m ⁻² min ⁻¹)	MTCR (pH gradient) (μg m ⁻² min ⁻¹)
12:00 a.m.	4	29.9	8.0	0.4	20.7	11.9	40.27	62.0	127.6
1:00 a.m.	4	29.5	8.0	1.2	21.6	11.9	39.68	62.0	127.5
2:00 a.m.	4	29.2	8.0	1.4	22.4	9.2	39.30	61.9	127.4
3:00 a.m.	4	28.9	8.0	1.0	21.0	9.2	38.96	61.8	127.2
4:00 a.m.	4	28.7	8.0	1.0	20.1	10.2	39.41	61.9	127.4
5:00 a.m.	4	28.5	8.0	1.0	19.9	11.8	39.62	62.0	127.5
6:00 a.m.	4	28.2	8.0	0.6	19.4	12.0	39.46	61.9	127.4
7:00 a.m.	4	28.1	8.0	1.2	20.4	10.0	39.84	62.0	127.5
8:00 a.m.	4	28.0	8.0	1.8	21.6	7.6	38.86	61.9	127.2
9:00 a.m.	4	27.9	8.0	2.0	22.6	6.6	35.94	61.4	126.3
10:00 a.m.	4	28.0	8.1	2.0	23.4	5.6	32.75	60.8	125.3
11:00 a.m.	4	28.3	8.1	2.3	24.3		31.75	60.7	124.9
12:00 p.m.	4	28.9	8.1	2.4	25.7	3.6	30.64	60.5	124.6
1:00 p.m.	4	29.1	8.1	1.6	26.5	3.3	30.32	60.4	124.5
2:00 p.m.	4	29.1	8.1	1.4	27.1	2.0	29.56	60.3	124.2
3:00 p.m.	4	29.5	8.1	1.3	27.5	2.9	28.87	60.2	124.0
4:00 p.m.	4	30.1	8.1	1.2	28.4	2.5	27.81	60.0	123.7
5:00 p.m.	4	30.2	8.1	1.3	28.4	2.4	27.48	59.9	123.6
6:00 p.m.	4	30.1	8.1	1.1	27.8	2.0	27.18	59.9	123.5
7:00 p.m.	4	29.6	8.1	0.6	25.7	1.8	32.21	60.7	125.1
8:00 p.m.	4	29.1	8.0	0.8	23.6	3.0	35.97	61.3	126.3
9:00 p.m.	4	28.9	8.0	0.3	21.4	3.6	37.92	61.6	126.9
10:00 p.m.	4	28.6	8.0	0.1	20.2	4.4	38.99	61.7	127.2
11:00 p.m.	4	28.4	8.0	0.4	19.3	4.5	39.87	61.9	127.5

Table 3

Seasonally averaged measured and modeled flux values

Sample dates	Sulfide (mg L ⁻¹)	Lagoon temperature (°C)	pH	Wind speed (m s ⁻¹)	Measured flux (μg m ⁻² min ⁻¹)	Modeled flux results		
						MTNCR (μg m ⁻² min ⁻¹)	MTCR I (pH constant) (μg m ⁻² min ⁻¹)	MTCR II (pH gradient) (μg m ⁻² min ⁻¹)
26 October–1 November 2004	0.6 ^a (0.3–1.5 ^b)	18.2 (15.7–23.3)	8.1 (8.0–8.2)	1.4 (0.1–4.0)	0.3	6	35	36
15–21 February 2005	3.2 (0.1–9.4)	11.5 (9.1–14.5)	8.1 (8.0–8.2)	1.7 (0.1–4.9)	~0.0	38	190	198
14–19 April 2005	1.8 (1.0–2.5)	15.1 (12.4–19.8)	8.1 (8.0–8.2)	2.9 (0.4–7.6)	0.5	19	106	110
14–18 June 2005	9.2 (4.0–13.0)	29.7 (26.9–32.5)	8.0 (7.9–8.1)	1.4 (0.1–2.9)	5.3	84	532	552

^a Seasonally averaged value.^b Seasonal range.

lagoon liquid, and determined that the dissociation constant values in lagoon liquid were ~50% of deionized water. Similar tests are needed to determine the rate dissociation constant for H₂S in similar conditions. Additionally, as discussed in Section 2.2.3, it has been shown by past researchers the liquid mass transfer coefficients may be significantly altered in different aqueous mediums. Decreasing the liquid mass transfer coefficient in each model produces an equivalent flux reduction. For example, applying a mass transfer coefficient that is reduced by 50%, leads to a 50% reduction in predicted emissions. Empirical equations based on wind tunnel experiments were used to calculate both gas and liquid mass transfer coefficients. These experiments were not conducted using hydrogen sulfide, so questions may

arise as to how well these equations apply to this model. An alternative approach to obtain these coefficients is to use a mechanistic approach; however, these equations do not consider wind speed, which may be an important parameter for emissions from a quiescent liquid surface.

In the process-based models presented in this paper, no other chemical or physical processes are considered that occur in the liquid phase. For example, gases such as ammonia and carbon dioxide (Aneja et al., 2000; Lim et al., 2003; Blunden and Aneja, 2008), and bacteria, e.g., bacteriochlorophyll *a*, which may oxidize hydrogen sulfide and consume ammonia (Byler et al., 2004) are present in swine waste treatment lagoons. This lack of inclusion in the model may also significantly affect predicted emission rates.

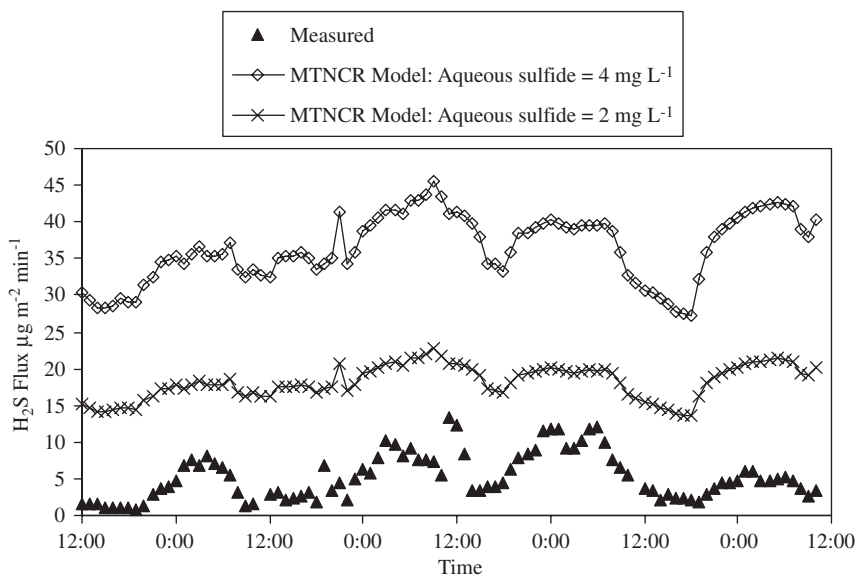


Fig. 4. Comparison of MTNCR Model flux predictions and dynamic flux chamber results for the summer experimental period (14–18 June 2005) with measured seasonally averaged aqueous sulfide concentration levels and 50% of measured seasonally averaged aqueous sulfide concentration levels.

For this work, an average value of 5×10^6 molecules cm^{-3} was used as a constant OH concentration value, based on values provided by Seinfeld and Pandis (1998); it is noted that although OH is ubiquitous in the atmosphere, concentrations may vary widely over time of day, location, and season. Upon model sensitivity analysis, however, it was found that varying the gaseous OH radical concentration by as much as an order of magnitude does not affect the predicted H_2S flux. The rate reaction constant for H_2S with the hydroxyl radical in the atmosphere therefore is not believed to affect the flux from this system.

Predicted modeled emissions were made based on average measured aqueous sulfide content in the lagoon during the experimental periods. It is noted that the range of sulfide concentration was quite large: for example, $0.3\text{--}1.5 \text{ mg L}^{-1}$, $0.1\text{--}9.4 \text{ mg L}^{-1}$, and $4.0\text{--}13.0 \text{ mg L}^{-1}$, during the fall, winter, and summer experimental periods, respectively. Also, grab samples were only collected during daytime hours 1–2 times per day during experimental periods and so it is unknown how much the concentration may change over the 24-h diurnal period. Combining the sensitivity analysis for aqueous sulfide concentration (Fig. 2c) and the diurnal variation (Fig. 3), Fig. 4 shows that lower average sulfide concentration values strongly affect the predicted H_2S flux. Lastly, data tested on these models is from a single source (although seasonal variation is included). The pH ranges in this system did not vary enough to thoroughly test the model with regard to this parameter. In the future, it would be useful to obtain additional data collected at various pH levels.

4. Conclusions

A processed-based mass transport model has been developed in an effort to predict hydrogen sulfide flux

from anaerobic waste treatment systems. Different conditions were considered, resulting in three variations of the model. The MTNCR Model considers mass transport and neglects chemical reactions. Two models consider mass transport coupled with chemical reaction in the gas and liquid phases (MTCR). The MTCR Model I assumes pH to be constant for mass transport through the liquid film, while the MTCR Model II considers a possible pH gradient in the liquid film.

For all models, the hydrogen sulfide flux is dependent on lagoon parameters including aqueous sulfide concentration, lagoon temperature and pH. It was observed that as temperature is increased in the system, flux decreases, due to the decreased dissociation of hydrogen sulfide. Ambient air temperature does not appear to affect emission rates. Wind velocities $<3.25 \text{ m s}^{-1}$ at 10 m height do not affect flux; however, at wind velocities $>3.25 \text{ m s}^{-1}$ an exponential increase in flux is predicted for all models. Hydrogen sulfide emissions are driven primarily by the liquid phase and it was found that varying the liquid film thickness significantly alters flux rates. The gas film thickness did not have an effect on flux.

The MTCR Models I and II predicted the highest increase in emission rates as aqueous sulfide concentration was increased. Model II predicted emissions ~4% higher than Model I. Both MTCR models predicted emission rate increase >6 times higher than MTNCR Model. The MTNCR Model showed the highest dependence on pH and the MTCR Model II shows a slightly lower flux increase rate as pH is decreased compared to the MTCR Model I.

All three models showed good agreement in diurnal comparison with flux measurements made using a dynamic flow-through chamber system during the summer. However, each model significantly over predicted the measured flux rates. The MTNCR Model estimates were

closest to experimental values, predicting 3–35 times the actual measured values. Limited data is available to test these models. It is recommended that additional data, obtained under different conditions (i.e., pH levels, and sulfide concentrations), be used to test and evaluate model performance in the future.

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