

ABSTRACT

BLUNDEN, JESSICA. Measurement, analysis, and modeling of hydrogen sulfide emissions from a swine facility in North Carolina. (Under the direction of Viney P. Aneja).

Annual global source contributions of sulfur compounds to the natural atmospheric environment are estimated to be 142×10^6 tons. Although not quantified, volatilization from animal wastes may be an important source of gaseous reduced sulfur compounds. Hydrogen sulfide (H_2S) is a colorless gas emitted during decomposition of hog manure that produces an offensive "rotten egg" odor. Once released into the atmosphere, H_2S is oxidized and the eventual byproduct, sulfuric acid, may combine with other atmospheric constituents to form aerosol products such as ammonium bisulfate and ammonium sulfate.

In recent years, confined animal feeding operations (CAFOs) have increased in size, resulting in more geographically concentrated areas of animals and, subsequently, animal waste. In North Carolina and across the southeastern United States anaerobic waste treatment lagoons are traditionally used to store and treat hog excreta at commercial hog farms. Currently, no state regulations exist for H_2S gaseous emissions from animal production facilities in North Carolina and the amount of H_2S being emitted into the atmosphere from these potential sources is widely unknown. In response to the need for data, this research initiative has been undertaken in an effort to quantify emissions of H_2S from swine CAFOs.

An experimental study was conducted at a commercial swine farm in eastern North Carolina to measure hydrogen sulfide emissions from a hog housing unit utilizing a mechanical fan ventilation system and from an on-site waste storage treatment lagoon. A

dynamic flow-through chamber system was employed to make lagoon flux measurements. Semi-continuous measurements were made over a one-year period (2004-2005) for a few days during each of the four predominant seasons in order to assess diurnal and temporal variability in emissions. Fan rpm from the barn was continuously measured and flow rates were calculated in order to accurately assess gaseous emissions from the system. Temperature at the fan outlet and static pressure inside the barn were measured. Lagoon samples were collected daily and analyzed for sulfide content. Lagoon parameters, temperature and pH; and atmospheric environmental parameters, ambient temperature, relative humidity, wind speed and ambient hydrogen sulfide concentration were concurrently monitored on-site. The highest barn emissions were measured during the winter and appeared to be related to the age and weight of the animals housed inside the barn. Highest lagoon emissions were measured in summer with higher sulfide content and warmer temperatures, which increase biological activity in the lagoon.

The mechanistic process of H_2S emissions from anaerobic liquid systems are investigated using three different modeling approaches based on the two-film theory of mass transfer: coupled Mass Transfer with Chemical Reactions Model (MTCR) with the assumption (1) pH remains constant in the liquid film (MTCR Model I), (2) pH changes from the bulk liquid phase to the air-liquid interface due to diffusion processes that occur within the film (MTCR Model II), and (3) absence of chemical reactions (MTNCR Model). Results of model predictions indicate that flux is primarily dependent on the physico-chemical lagoon properties including sulfide concentration, pH, and lagoon temperature. Low wind velocities (i.e., $U_{10} < 3.25 \text{ m s}^{-1}$) and air temperature have little

impact on flux. The flux was also influenced by variations in the liquid film thickness, signifying that the H_2S flux is driven by resistance in the liquid-phase. Model results were compared with H_2S flux measurements in order to evaluate the models' accuracy in calculating lagoon H_2S emissions. All three models showed good qualitative agreement in diurnal comparison (i.e., predicting flux patterns as meteorological and lagoon conditions varied throughout the day) with flux measurements made using a dynamic flow-through chamber system during the summer. However, each model significantly over predicted the measured flux rates.

**MEASUREMENT, ANALYSIS, AND MODELING OF HYDROGEN SULFIDE
EMISSIONS FROM A SWINE FACILITY IN NORTH CAROLINA**

by

JESSICA BLUNDEN

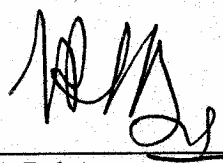
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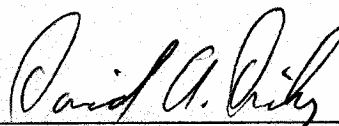
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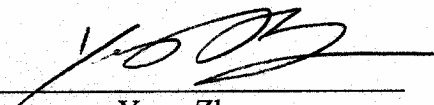
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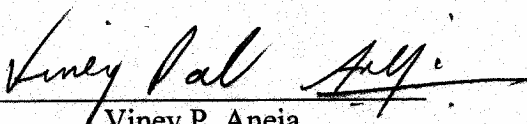
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BIOGRAPHY

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After moving to Asheville, North Carolina in 1995, Jessica decided to pursue her long-time interest in environmental issues and atmospheric science. She attended the University of North Carolina at Asheville for three years and, combining her two interests, Jessica entered graduate school at North Carolina State University in August 2001 as a member of the Air Quality Research group. Her M.S. research focused on field monitoring, specifically the characterization of volatile organic compounds at confined animal feeding operations. In 2003, she received her M.S. in Atmospheric Sciences and decided to further pursue her Ph.D. in the same program. Upon completion of her Ph.D., Jessica has been appointed to a one-year postdoctoral position at NC State University to continue research in air quality field monitoring and measurements.

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This research would not be possible without the cooperation of the Frontline Farmers Association, who allowed us to use the commercial farm to conduct our research. I thank our field technician, Wesley Stephens, and the Air Quality Research Group for their assistance with the field experiments, and especially for driving 200 miles with me every day to the experimental site during the field seasons. I also give many thanks to Brian Baldelli, who went above and beyond the call of duty to drive our gas cylinders to and from the site during each season. I wish to thank Roberto Munilla, Kim Kasdorf, and the NC State University Machine Shop for their assistance in various aspects of the experimental technical design. The North Carolina Division of Water Quality generously offered their services to analyze all of our aqueous liquid samples.

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NOTATIONS

$[H^+]$	Concentration of hydrogen ion in aqueous solution (mole L ⁻¹)
A	Surface area covered by chamber (cm ²)
A_w	Inner surface area of the chamber (cm ²)
C	H ₂ S concentration inside the chamber (ppbV)
C_{air}	H ₂ S concentration in carrier air (ppbV)
C_a	Concentration of hydrogen sulfide in bulk air phase (mole L ⁻¹)
C_{ai}	Concentration of hydrogen sulfide at air-liquid interface for air phase (mole L ⁻¹)
C_{H_2S}	Concentration of hydrogen sulfide in aqueous solution (mole L ⁻¹)
C_{HS^-}	Concentration of bisulfide ion in aqueous solution (mole L ⁻¹)
C_L	Concentration of hydrogen sulfide in bulk liquid phase (mole L ⁻¹)
C_{Li}	Concentration of hydrogen sulfide at air-liquid interface for liquid phase (mole L ⁻¹)
$C_{S=}$	Concentration of sulfide anion in aqueous solution (mole L ⁻¹)
C_{TS}	Concentration of total sulfide in aqueous solution
D_a	Diffusivity of hydrogen sulfide in the air (cm ² s ⁻¹)
D_{ether}	Diffusivity of ethyl ether in the liquid (cm ² s ⁻¹)
$D_C(D_{H_2S})$	Diffusivity of hydrogen sulfide in the liquid (cm ² s ⁻¹)
$D_E(D_{HS^-})$	Diffusivity of bisulfide ion in the liquid (cm ² s ⁻¹)
$D_F(D_{H^+})$	Diffusivity of hydrogen ion in the liquid (cm ² s ⁻¹)
D_w	Diffusivity of a gas in water (cm ² s ⁻¹)
$D_{w,25}$	Diffusivity of a gas in water at 25°C (cm ² s ⁻¹)
E_L	Concentration of bisulfide ion in bulk liquid phase (mole L ⁻¹)
E_{Li}	Concentration of bisulfide ion at air-liquid interface for liquid phase (mole L ⁻¹)
f	Fan flow rate
F_L	Concentration of hydrogen ion in bulk liquid phase (mole L ⁻¹)
F_{Li}	Concentration of hydrogen ion at air-liquid interface for liquid phase (mole L ⁻¹)
h	internal height of the chamber (cm)
H	Henry's Law constant (mol L ⁻¹ _(g) / mol L ⁻¹ _(l))
J_a	Hydrogen sulfide flux in gas phase (µg m ⁻² min ⁻¹)
J	lagoon emission flux per unit area (µg m ⁻² s ⁻¹)
J	barn emission rate (µg m ⁻³)
J_{ai}	Hydrogen sulfide flux at air-liquid interface for air phase (µg m ⁻² min ⁻¹)
J_L	Hydrogen sulfide flux in liquid phase (µg m ⁻² min ⁻¹)
J_{Li}	Hydrogen sulfide flux at air-liquid interface for liquid phase (µg m ⁻² min ⁻¹)
k_a	Gas mass transfer coefficient (cm s ⁻¹)
k_L	liquid mass transfer coefficient (cm s ⁻¹)
k_{ra}	Overall reaction rate constant for reaction of hydrogen sulfide in air (s ⁻¹)
$K_{a,1}(K_L)$	Acidity (rate dissociation) constant for hydrogen sulfide (mole L ⁻¹)
$K_{a,2}$	Acidity (rate dissociation) constant for bisulfide ion (mole L ⁻¹)
K_{OL}	overall mass transfer coefficient (cm s ⁻¹)

L	Loss of H_2S in the chamber per unit area ($m\ min^{-1}$)
q	flow rate of compressed air through the chamber (lpm)
r_a	$\sqrt{k_{ra} / D_a}$
R	gas phase reactions inside the chamber
S_{ca}	Schmidt number in the air (dimensionless)
S_{cL}	Schmidt number in the liquid (dimensionless)
t_a	Air phase film thickness (cm)
t_L	Liquid phase film thickness (cm)
T_L	Lagoon temperature ($^{\circ}C$)
T_a	Air temperature ($^{\circ}C$)
U_{10}	Wind speed at 10 m reference height ($m\ s^{-1}$)
U_*	Friction velocity ($m\ s^{-1}$)
V	Volume of the chamber (L)
ρ_a	Density of moist air ($g\ cm^{-3}$)
ρ_w	Density of water ($g\ cm^{-3}$)
μ_a	Dynamic viscosity of air ($kg\ m^{-1}\ s^{-1}$)
μ_w	Dynamic viscosity of water ($g\ cm^{-1}\ s^{-1}$)
ν_a	Kinetic viscosity of air ($cm^2\ s^{-1}$)
ν_w	Kinetic viscosity of water ($cm^2\ s^{-1}$)
Σ	Summation

CHAPTER I. INTRODUCTION

Emissions of odor, ammonia, (NH₃), and gaseous sulfur compounds from animal (swine) and poultry waste has become a significant problem, both political and environmental, owing to the enhanced pork and poultry production (Aneja et al., 2006a). In North Carolina, hog farming is now a primary agricultural industry in the state, accounting for revenues in excess of \$2 billion per year. According to the North Carolina Department of Agriculture (NCDA) and Consumer Services, between 1987 and 1997 the number of hogs in North Carolina increased sharply from an inventory of 2.5 million to ~10.1 million head (NCDA, 2004). [The hog growth ceased in 1997, due to a moratorium imposed on any new or existing hog farms in the state by the North Carolina State Legislature (House Bill 515; S.L.1997-458)]. As the hog population increased over time, the number of hog operations decreased in parallel, from 13,500 in 1987 to 2,400 by 2005. Consequently, more hogs are confined to fewer farms and, due to a higher amount of excretion, likely increasing the amount of odorous and potentially harmful compounds released into the atmosphere at these locations. The vast majority of the hog farms are located in the southeastern coastal plain region of North Carolina (Figure 1.1).

Environmental concerns and complaints regarding air and water quality associated with the increased number of animals and management of subsequent wastes accompanying the growth of this industry have been considerable. While significant efforts have been devoted to understanding emissions of ammonia from these operations (Aneja et al., 2000, 2001a,b), there remains a lack of information concerning the emissions of gaseous sulfur compounds.

Figure 1.2 depicts the most current (2002) emissions inventory for hydrogen sulfide (H_2S) in North Carolina, determined by the North Carolina Division of Air Quality (NC DAQ). Emissions from animal feeding operations are not included, primarily because air emissions inventories are not required from this industry and therefore no data is available. For U.S. Environmental Protection Agency (EPA) (2001) H_2S emission factors applied to NC hog farms, it is projected that there would be over 40 million lb yr^{-1} emitted from hog operations, or over three times the emission amount from the fertilizer and pulp/paper industries combined (Schliesser, 2003). Assuming that the EPA emission factor data were appropriate (*draft report based only on midwest farms from unpublished data*), the NC DAQ modeled an actual, representative NC farm with 4,000 hogs. Results showed that the farm would be in compliance with the H_2S 24 hr acceptable ambient level (AAL) of 83 ppb (0.12 mg m^{-3}). The NC DAQ believes that the EPA H_2S emission factors significantly over-estimate H_2S releases from NC hog farms due to differences in determining emissions parameters (i.e., lagoon pH values) but concede that a large data gap exists.

1.1 Background

1.1.1 The Sulfur Cycle

There are substantial natural emissions of sulfur compounds into the troposphere. Anthropogenic emissions consist almost entirely of sulfur dioxide (SO_2), whereas natural emissions are mainly in the form of reduced sulfur compounds (Finlayson-Pitts and Pitts, 1986). The major reduced volatile sulfur compounds consist of hydrogen sulfide (H_2S), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), carbonyl sulfide (COS), carbon disulfide (CS_2), methyl mercaptan (CH_3SH), and ethyl mercaptan ($\text{C}_2\text{H}_5\text{SH}$). In previous

studies, these compounds have been measured in biological activity in vegetation, soils, and water ecosystems (Hill et al., 1978; Aneja et al., 1979, Aneja et al., 1981, Aneja and Overton, 1990, Bandy et al., 1992; Andrae et al., 1993; Johnson et al., 1993; Cooper and Saltzmann, 1993; Pio et al., 1996; Bodenbender et al., 1998; Turner et al., 1998; Kim et al., 2004). Figure 1.3 provides a schematic representation of the sulfur cycle and Table 1.1 lists calculated fluxes for the global atmospheric sulfur cycle.

1.1.2 Sources and Sinks of Gaseous Reduced Sulfur Compounds

Total reduced sulfur is the combined load of major reduced volatile sulfur compounds naturally emitted into the atmosphere. Total reduced sulfur may therefore be defined as S_x where,

$$S_x = H_2S + DMS + DMDS + COS + CS_2 + CH_3SH + C_2H_5SH \quad (1)$$

Hydrogen sulfide is the main reduced sulfur compound emitted from the continents and from plants, and has a significant source from the marine environment (Andreae, 1990). Other sources include salt marshes/estuaries/tidal flats, vegetation, tropical forest wetlands, volcanoes, and atmospheric reaction between COS and OH (Warneck, 2000). The major atmospheric chemical reaction sink for H_2S is via reaction with the hydroxyl radical (OH) in the atmosphere.

Dimethyl sulfide is believed to be the major reduced sulfur gas released from the oceans (Andreae, 1990). Dimethyl sulfonium propionate (DMSP) is released from algae and converted to DMS by cleavage with the secondary S-C bond, and is thought to be mediated by biological or biochemical means rather than chemical means (Kelly and Smith, 1990). This gas is very insoluble and is therefore degassed quickly into the atmosphere (DeBruyn et al., 1995). Other sources include salt marshes/estuaries,

vegetation, tropical forests, soils, wetlands, and anthropogenic sources. It is believed that the main atmospheric chemical reaction sinks of DMS are due to the reaction with OH during the daytime, and the reaction with the nitrate radical (NO_3) during the nighttime (Wilson and Hirst, 1996).

Salt marshes and estuaries appear to be rich sources of CS_2 (Watts, 1991). The primary sources for CS_2 are believed to be rotting organic matter. Other sources include anoxic soils, wetlands volcanoes, and anthropogenic sources (Chin and Davis, 1995; Xie et al., 1997). There are few oceanic measurements of CS_2 ; however, the literature available suggests that emissions follow the same general pattern as COS, with higher concentrations in coastal waters and less in the open ocean (Xie et al., 1997). CS_2 displays a maxima in both the free troposphere and the boundary layer. This is an indication that the ocean is not likely to be the primary source of global CS_2 (Cooper and Saltzman, 1993). Once airborne, it is quickly transformed to COS and SO_2 through reaction with OH radical (Chin and Davis, 1993). Another sink for CS_2 is oxic soils (Watts, 2000).

Global sources of COS include oceans, anoxic soils, wetlands, volcanoes, precipitation, DMS and CS_2 oxidation, biomass burning, and anthropogenic sources (Warneck, 2000). The most significant tropospheric source of COS appears to be the photochemical oxidation from CS_2 (Watts, 2000), which contributes equal amounts of COS and SO_2 . The oxidation of DMS by OH radical also produces COS in a side reaction (Barnes et al., 1994). Major sinks include oxic soils and vegetation. Other sinks include photochemical reactions with OH and O, and photolysis (Watts, 2000).

Methyl mercaptan is emitted from plants that contain the amino acids, cysteine and methionine, and are involved in the metabolism leading to the emission of this compound (Warneck, 2000), as well as tidal mud flats, salt marshes and soils. Dimethyl disulfide has also been determined to be emitted from tidal flats, marshes, and soils (Warneck, 2000). The photooxidation of these compounds with OH serve as the primary atmospheric chemical reaction sinks in the troposphere.

Annual source contributions of sulfur compounds in the natural atmospheric environment are estimated to be 142×10^6 tons, mainly in the form of H_2S , DMS, DMDS, COS, CS_2 , and CH_3SH (Warneck, 2000). Table 1.2 provides emissions estimates for natural sources of selected sulfur compounds (H_2S , DMS CS_2 , and COS) in the atmosphere. Note that there is no estimate provided for sulfur emissions from animal waste and/or production facilities, similar to the North Carolina 2002 H_2S emissions inventory. Volatilization from animal wastes may be an important source of gaseous reduced sulfur compounds, particularly in eastern N.C. where the swine industry constitutes a major agricultural activity.

1.1.3 Biogenic Sulfur Production

The sulfur gases of biogenic origin are produced by, yet an unclear mechanism, certain bacteria. Work performed on the production of H_2S suggest that it is generated by bacteria in two ways: by dissimilatory sulfate reduction and by dissimilatory reduction following protein decomposition. Dissimilatory sulfate bacteria grow at the expense of a variety of organic compounds (Pezet and Pout, 1977), and in so doing they utilize sulfate and other inorganic sulfur compounds as terminal electron receptors in much the same way that aerobic bacteria utilize oxygen (Postgate, 1959). These organisms, restricted to

the genera, are strictly anaerobic and may be found in water and sediments and in terrestrial soils.

In the second mode of H_2S generation, the source of sulfur is the reduced form into which it is converted upon assimilation into living matter. The sulfur containing amino acids make up the bulk of organic sulfur constituents of living cells. Release of sulfide from such organic sulfur compounds, resulting in so-called nonspecific sulfide reduction, is a widespread property among bacteria (LaRiviere, 1966). Such organisms may be found in both aerobic and anaerobic environments, especially those containing large amounts of readily decomposable organic matter.

If, in the course of bacterial sulfate reduction, ferrous iron or heavy metals are present, insoluble metallic sulfides will be produced and no H_2S will be formed. Upon exhaustion of these metals, H_2S will be produced. It will then be transported by turbulent diffusion and other mixing processes to the air-water interface where it is released to the atmosphere.

During transport through water, H_2S is subject to oxidation principally by dissolved oxygen but also by bacterial action. Rates of reaction have been studied in the laboratory and field experiments by Skopintsev et al. (1959, 1964), Ostlund and Alexander (1963), Cline and Richards (1969), and Chen and Morris (1972a,b). The induction periods, the complex dependence of reaction to impurities, the number of intermediates and their products, and the dependence of the initial specific rate on pH all indicate a lack of simplicity.

According to the U.S. EPA (2001), under anaerobic conditions, any excreted sulfur that is not in the form of H_2S will be reduced microbially to H_2S . Therefore,

manures managed as liquids or slurries are potential sources of hydrogen sulfide emissions. The microbiologic reduction of sulfate to hydrogen sulfide is accomplished by members of two genera of anaerobic bacteria: *Desulfovibrio* (five species) and *Desulfotomaculum* (three species). These bacteria are strictly anaerobic, heterotrophic, and have a respiratory metabolism in which sulfates, sulfites, and other reducible sulfur compounds serve as the final electron receptors, with the resultant production of hydrogen sulfide (NRC, 1979). However, heavy growths of purple sulfur bacteria (PSB) of the family Chromatiaceae may occur in anaerobic waste treatment lagoons where hydrogen sulfide is actively oxidized by these bacteria (NRC, 1979), adding to the complexity of these systems.

1.1.4 Environmental/Climatic Impacts

Many sulfur compounds are associated with unpleasant odors. Sensory characteristics for several reduced sulfur gases, along with their respective odor thresholds, are listed in Table 1.3. Odor threshold can be defined as the concentration at which odor is first detected. According to Schiffman et al. (2001), irritancy occurs at 3-10 times higher concentration than the odor threshold. Although the individual species may not exceed the concentration known to cause irritation, often the combined load of compounds may exceed the irritation threshold (Korpi et al., 1999). Odor complaints have increased rapidly with the increase in the number of swine production facilities (Schiffman et al., 2001). Odor sources include animal confinement houses, anaerobic storage lagoons, and spray fields adjacent to the properties that utilize waste or effluent as a means of fertilization treatment on crops (U.S. EPA, 2001).

Adverse health symptoms can occur at concentrations that are above odor detection thresholds but well below the levels that cause irritation (Schiffman, 2001). Potential negative health effects have been identified in production workers and neighboring residents that include respiratory illnesses such as bronchitis and asthma, and increased psychological stress (Schiffman, 1998). Campagna et al. (2004) have reported a correlation between elevated ambient H₂S concentrations and hospital visits for respiratory diseases.

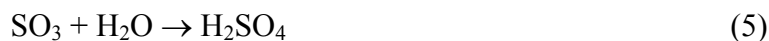
Gaseous sulfur is one of the main chemical species involved in the gas-to-particle conversion process. The more labile compounds, H₂S, DMS, DMDS, CH₃SH, C₂H₅SH and CS₂, have relatively short atmospheric residence times upon release into the ambient air. As a result, mixing ratios fluctuate significantly and decrease rapidly with distance from the locale of origin (Warneck, 2000). Large diurnal variations have been associated with DMS and CH₃SH. Observations suggest that these compounds are highly reactive with the nitrate (NO₃) radical, which becomes active during nighttime and is likely the source of a major loss process (Warneck, 2000). Atkinson and Carter (1984) found that the reactions of reduced sulfur species with ozone (O₃) are too slow to be considered significant. These sulfur compounds are mainly oxidized by tropospheric OH to form SO₂. On the other hand, COS is a relatively inert gas. Owing to its extended lifetime, it is the most abundant sulfide in the atmosphere and is evenly distributed throughout the troposphere (Warneck, 2000). Table 1.4 provides an estimate of the lifetimes for the reactions of specified reduced sulfur compounds with OH and NO₃ radicals (Finlayson-Pitts and Pitts, 1986).

Each of the reduced sulfur compounds undergoes a different complex series of atmospheric chemical reactions, eventually oxidizing to form SO₂. For example, H₂S is believed to proceed via hydrogen atom abstraction,

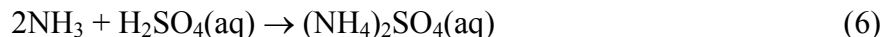


with the HS radical further reacting to form SO₂ (Cox and Sheppard, 1980).

The dominant gas phase pathways for sulfuric acid (H₂SO₄) are:



Atmospheric gas phase reactions may lead to the formation of condensable products that associate with the atmospheric aerosol. Gaseous H₂SO₄ may then be neutralized by ammonia to form sulfate salts (Warneck, 2000):



Aneja et al. (1998) estimated that 68,540 tons of NH₃ are emitted from swine facilities annually in North Carolina.

The chemical reactivity of atmospheric ammonium sulfate relies largely on the particle phase. This phase also is important in determining the ability of the particle to serve as an effective cloud condensation nucleus. The vapor pressures of NH₃ and H₂SO₄ in equilibrium are much lower than that of sulfuric acid in the presence of water (Scott and Cattell, 1979). This lowers the critical cluster size and thus enhances the rate of nuclei formation (Warneck, 2000).

Particles produced in gas-to-particle conversion reactions at ambient temperatures tend to be in the Aitken nuclei size range, with diameters $\leq 0.08 \mu\text{m}$ (Claes, 1998).

Particles in this size range efficiently act as nuclei for the condensation of low vapor gaseous species or quickly coagulate, thus forming accumulation mode particles in the range of 0.08-2.0 μm (Claes, 1998). Accumulation mode particles have longer residence times and can be incorporated into cloud droplets, then are removed by washout or rainout. The extended lifetime of the particle allows for further transport and deposition from the source locale. Particulate ammonium sulfate has a residence time of ~1-15 days, owing to a decrease in dry deposition velocity (Aneja et al., 1998).

Ammonium sulfate in the atmosphere may create a regional cooling effect by scattering incoming light radiation (Lightstone et al., 1999). An environmental hazard in eastern North Carolina associated with the ammonium sulfate aerosol is deposition into sensitive coastal river systems such as the Pamlico-Albemarle Sound, Neuse River Basin, and Cape Fear Watershed where nitrogen loading may lead to enhanced eutrophication and soil acidification, which may in turn upset plant nutrient balances near sources (Paerl, 1997).

1.1.5 Reduced Organic Sulfur Compounds at CAFOs (Swine)

Characterizing gaseous sulfur emissions from large-scale animal production facilities in North Carolina requires an understanding of the multiple source terms and temporal patterns in animal production that exist for each type of operation. Confinement facilities, manure storage tanks, ponds, anaerobic lagoons, and land application sites are primary sources of hydrogen sulfide emissions whenever sulfur is present in manure (U.S. EPA, 2001). There are two primary sources of sulfur in animal manures: sulfur amino acids contained in the feed and inorganic sulfur compounds (i.e., copper sulfate and zinc sulfate) which are used as feed additives to supply trace minerals and serve as

growth stimulants (U.S. EPA, 2001). The potential to emit hydrogen sulfide will be greatest when manure is handled as a liquid or slurry. High temperatures, pH values < 7.0, and manure residence times are all factors that increase H₂S emission (U.S. EPA, 2001).

O'Neill and Phillips (1992) and Schiffman et al. (2001) have qualitatively identified H₂S, CH₃SH, C₂H₅SH, DMS, CS₂, COS, DMDS as present in the ambient air in these types of rural environments (i.e., Confined Animal Feeding Operations, CAFOs). Kuroda et al. (1996) have measured H₂S, CH₃SH, DMS, and DMDS from fresh swine feces during composting in a laboratory study.

A few studies have quantified some reduced organic sulfur mixing ratios and emissions from swine confinement houses and soils where hog manure has been applied (Table 1.5). Emissions from rice paddies soils utilizing organic manure from hogs demonstrated that, when comparing the two different fertilizer types for CH₃SH, (i.e., paddies using organic manure and chemical fertilizer, and paddies using only chemical fertilizer), there is a higher emission rate from the paddies using only chemical fertilizer. When comparing the two different fertilizer types for DMDS there is a higher emission rate from the paddies using both chemical fertilizer and organic manure, suggesting that DMDS may be more likely to have a source in hog manure than CH₃SH. In the rice paddy study, Yang et al (1998) also determined that higher emissions of DMS and CS₂ occurred from soils using organic manure (from hogs) and chemical fertilizer rather than chemical fertilizer alone. Emissions of COS were slightly lower from soils using only applied chemical fertilizer. H₂S was not detected (or was below detectable limits) when both hog manure and chemical fertilizer were applied.

Heber et al. (1997) measured H₂S emissions from two naturally ventilated swine finishing building in Indiana. Ni et al. (2002) measured summertime emissions of H₂S at a mechanically ventilated swine finishing building in Illinois. In this study, it was determined that concentrations inside the building were 173 ppbV and emissions were ~578 g day⁻¹ (or ~8 g day⁻¹ 500kg Live Animal Weight (LAW)⁻¹). It should be noted that the inside of the building is not subject to ambient meteorological variables (i.e., temperature, wind speed, PBL depth, atmospheric stability, etc.), which generally play a key role in the ambient mixing ratios.

Clanton and Schmidt (2000) reported DMS, DMDS, CH₃SH, CS₂, and COS concentrations in the headspace above a deep pit at a swine facility in Minnesota. Using a Tedlar bag collection method, CS₂ showed highest concentrations and CH₃SSCH₃ showed the lowest concentrations (H₂S was measured using a Jerome meter but the results were questionable since other sulfur compounds may possibly be detected along with this compound). Lim et al. (2003) measured H₂S emissions from two anaerobic storage lagoons during the spring and summer months (Figure 1.4). Mean flux for H₂S among the two lagoons was 5.7 µg m⁻² s⁻¹ with an average pH value of 7.9 and average surface lagoon temperature of ~25°C; however, these measurements did not appear to be continuous and no diurnal or seasonal variation was reported. It should be noted that these studies were conducted in Midwest regions where lagoon parameters are likely different than those in the southeastern U.S. Limited attempts have been made to quantify and identify direct atmospheric emissions of gaseous sulfur compounds from hog production in this region. In addition, temporal, seasonal, and diurnal variations of these types of emissions have not been addressed in previous studies.

1.2 Methods and Materials

1.2.1 Physiographic Location and Farm Description

The experimental site is a commercial swine finishing farm, located in Jones County near Kinston, NC (Figure 1.5). The facility utilizes a conventional technology as its primary means of handling effluent, commonly referred to as a “Lagoon and Spray Technology” and is of the same type that is currently used by most farms in North Carolina. Effluent is released directly from the hog barns once a week into an on-site waste storage/treatment lagoon. The lagoon wastewater is periodically used to “recharge” the shallow pits under the slatted floor in the houses and also used as spray over on-site agricultural crops for nutrient enrichment purposes. The storage lagoon is 3.063 ha (30,630 m²) and the farm maintains eight houses on site, each with a fan tunnel ventilation system. A schematic layout of the site is depicted in Figure 1.6.

1.2.2 Sampling Scheme

Semi-continuous H₂S emissions measurements were made from the anaerobic swine waste treatment lagoon and a randomly selected barn on site during the four predominant seasons (i.e., summer, fall, spring, and summer) for a one year period. Samples were collected for ~5-7 days from both the lagoon and the confinement house during each field initiative. Measurements were made at the lagoon using a dynamic flow-through chamber system. A sample line was placed directly in front of a 91 cm diameter ventilation fan to measure gas concentration at the barn.

1.2.3 Barn Measurements

One barn, located furthest north on the property, was selected for measurements. Five AAA Associates Inc. Maxi-Brute™ fans with plastic shutters (Niles, MI), two 91

cm diameter direct-driven and three 122 cm diameter belt-driven, were located at the west end of the building. The fans were staged to operate as temperature increased inside the building.

1.2.3.1 System Design

A 1/4" o.d., 5/32" i.d. Teflon sample line was inserted inside the chimney of the first 91 cm fan to turn on, between the shutter and fan blade, at roughly half the fan radial distance. Due to the nature of the airflow through the building, it is assumed that the gaseous concentrations are uniformly distributed at each fan outlet. The air is drawn through the system and is then split using a Swagelok® stainless steel Union Tee in order to deliver the sample simultaneously to the analysis instruments.

In order to determine fan rpms, a Mabuchi VDC motor (Santa Clara, CA) was either (1) mounted to a stainless-steel plate configured to fit over the front of the 91 cm fan plate or (2) attached to a cylinder sleeve which fit over the fan shaft of the 122 cm fans. Single analog output wires were connected from each motor to a Campbell Scientific CR10X data logger (Logan, UT) which continuously recorded the measured voltage output every second and averaged the data over a fifteen minute timeframe. Prior to the experiment, each motor was calibrated in the laboratory to obtain voltage outputs at a specific rpm. For this process, each VDC motor was attached to the shaft of a Dayton SCR Controlled DC Motor (Model # 2M168C). A Shimpo DT-725 Stroboscopic Digital Tachometer and Shimpo DT-207B Direct Contact Digital Tachometer (Itasca, IL) were used to determine revolutions per minute (rpm) and a Micronta Digital Multimeter (Model # 22-185) was used to simultaneously determine voltage output at the respective

rpm. The rpm for each fan as well as “on/off” times could then be determined and flow rates subsequently calculated.

The pressure differential between the inside of the barn and the outside ambient air affects the air flow from the fans. The static pressure inside the building was monitored during the spring season using a Model PX655 Omega pressure transducer to measure the pressure difference between the inside of the barn (placed away from any wind currents) and the outside ambient air (tubing housed inside the mobile laboratory).

The flow rates for each fan size were calculated using the following calculation

$$CalculatedFlowRate = \left(\frac{ManufacturerFanFlowRate}{SpecifiedRPMs} \right) (MeasuredRPMs) \quad (7)$$

where the manufacturer fan flow rate was adjusted to the average static pressure measurements.

1.2.3.2 Emission Rate Calculation

The concentration distribution of the gases was assumed to be uniform across the front of the barn where the fans are located. Background samples of gases collected in 10-L Tedlar® bags over a five-minute timeframe were determined to be ~0-4% of the measured concentration at the fan outlet. Due to these low measurements, background concentrations were not considered for emission calculation. The barn emission rates are therefore calculated by the following equation:

$$J = C * \sum f \quad (8)$$

Where C is the measured gas concentration at the fan outlet and $\sum f$ is the sum of the calculated flow rates for each fan.

1.2.4 Lagoon Measurements

1.2.4.1 Dynamic Flow-Through Chamber System

The dynamic flow-through chamber system is a technique that has been developed and modified over the past 25 years in an effort to measure earth-atmosphere and water-atmosphere fluxes of various compounds including biogenic sulfur, oxides of nitrogen, ammonia, and methane. For measuring emissions, the chamber technique has the important advantage of association of a particular emission site and its measurable array of physical, chemical, and microbiological properties with emissions of particular compounds or their reaction products. In addition, gas residence times in the chamber are on the order of minutes so that chemical transformations between emission and analysis may be minimized (Aneja et al., 2006b).

A flow-through dynamic chamber system with a variable-speed motor-driven continuous impeller stirrer (Kaplan et al., 1988; Kim et al., 1994; Chauhan, 1999; Aneja et al., 2000) was used to determine H₂S flux from the lagoon surface. The translucent plastic cylindrical chamber, 26.4 cm internal diameter, 46.6 cm internal height of chamber above water or soil, and volume 25.4 L, was fitted into a circular hole cut into the center of a 0.61 by 0.61 meter floating ½” thick ultra-high molecular weight (UHMW) polyethylene platform which will penetrate into the lagoon ~7 cm. The platform was supported by 6” diameter by 5.5’ length PBC piping for floatation. A photograph of the chamber system floating on the lagoon is shown in Figure 1.7 and a schematic of the entire dynamic flow-through chamber system is depicted in Figure 1.8. In order to create an internally closed chamber system, a seal was formed between the chamber and the lagoon. The chamber was internally lined with a 2 mil fluorinated

ethylene propylene (FEP) Teflon sheet to reduce chemical reactions and build up of temperature inside the chamber. Compressed zero-grade air (used as a carrier gas) was pumped through the chamber at a variable flow rate of $\sim 9\text{--}12\text{ L min}^{-1}$ utilizing a Model 810-S Mass Trak Flow Controller (Sierra Instruments, Monterey, CA). The in-flowing air was passed through a $\frac{1}{4}$ " o.d., $\frac{5}{32}$ " i.d Teflon FEP sample line to the chamber. The air inside the chamber was ideally well-mixed by a variable-speed motor-driven Teflon impeller stirrer ranging from speeds of 40-60 rpm for this study. Roelle (1996) determined that varying the speed of the impeller stirrer did not produce any significant changes in calculated NO soil flux using this same type of methodology. Based on the impeller stirrer design, it is expected that the air flow characteristics inside the chamber at the air-water interface are similar to ambient air, i.e., flow outside the chamber, once steady-state has been reached (Perry and Chilton, 1973). The vent line attached to the sample line exiting the chamber minimizes the pressure difference between the inside of the chamber and the outside ambient air.

A vent line was fitted to the exiting sample line to prevent pressurization and was periodically bubble tested to check for under pressurization and/or leaks in the enclosed system. Sample lines did not exceed 10 meters. The entire closed system was lined with Teflon inside the chamber and stainless steel fittings in order to minimize chemical reactions with sample flow. Arkinson (2003) determined the relationship between the carrier gas flow rate and the flow speed within the chamber (chamber wind speed) at impeller speeds of 40 rpm and 60 rpm (Figure 1.9). The flow speed was measured at the height of the impeller stirrer ($\sim 0.5\text{ m}$ above the lagoon surface). It was found that calculated wind speeds range from 0.95 m s^{-1} to 1.93 m s^{-1} ; however, they are less

variable than wind speed outside the chamber due to the stability of the constant gas flow. The chamber wind speeds fell within the range of wind speeds estimated outside in the ambient air at 0.5 m height above the lagoon surface.

During this study the lagoon temperature was measured both inside the chamber system and ~0.3 meters outside the chamber, both at depths of ~6-7 cm beneath the lagoon surface. For all measured 15-minute averaged data ($n = 2017$), average lagoon near-surface temperatures were 17.9 ± 6.5 and 18.0 ± 6.6 °C inside and outside of the chamber system, respectively. The correlation was very strong between the two measurements ($r^2 = 0.998$); however there was a statistically significant difference ($p < .0001$). Minimum temperatures measured were the same for both locations, 9.1°C, while the maximum value was higher for the lagoon temperature outside the chamber (35.0°C) compared to the lagoon temperature inside the chamber system (32.8°C). The maximum difference between the two temperatures 3°C, measured during the winter season.

For this experiment, the platform design has been modified so that the dimensions of the platform are 0.61 by 0.61 meters as opposed to 1.3 by 1.3 meters used in previous experiments (Aneja et al., 2000; Arkinson, 2003; Semunegus, 2003) and the platform itself was designed to sit a few centimeters above the lagoon (rather than resting on top) in order to minimize experimental effects and simulate atmospheric conditions at the lagoon surface as accurately as possible. The chamber volume above water does not change with respect to this modification. The sample exiting the chamber travels through the sample line and is split in order to deliver the sample simultaneously to the analysis instruments.

1.2.4.2 Lagoon Flux Calculation

In order to calculate H₂S flux for this research experiment, the following mass balance equation was used for the dynamic flow-through chamber system:

$$\frac{dC}{dt} = \left(\frac{q[C_{air}]}{V} + \frac{JA}{V} \right) - (C) \left(\frac{LA_w}{V} + \frac{q}{V} \right) - R \quad (9)$$

where	C	H ₂ S concentration inside the chamber (ppbV)
	C_{air}	H ₂ S concentration in carrier air (ppbV)
	q	flow rate of compressed air through the chamber (lpm)
	V	volume of the chamber (25.4 L)
	A	surface area covered by chamber (545.3 cm ²)
	A_w	inner surface area of the chamber of inner and upper wall Surfaces (3849.3 and 545.3 cm ² , respectively)
	L	total loss of H ₂ S in the chamber per unit area (m min ⁻¹) due to reaction with inner and upper walls of the chamber
	h	internal height of the chamber (46.6 cm)
	J	emission flux per unit area (μg H ₂ S m ² s ⁻¹)
	R	gas phase reactions inside the chamber

Zero-grade air was used as the carrier gas, so C_{air} is to equal zero and gas phase reactions, R, are also assumed to be zero. Since the air inside the chamber is assumed to be well mixed by the impeller stirrer, C is assumed to be constant within the chamber. At steady-state conditions, the change of concentration with respect to time $\left(\frac{dC}{dt} \right)$ will be zero.

Therefore equation (9) can be simplified as:

$$\frac{J}{h} = C_{eq} \left(\frac{LA_w}{V} + \frac{q}{V} \right) \quad (10)$$

Loss term, L , is determined experimentally while equilibrium-state hydrogen sulfide concentration (C_{eq}), flow rate (q), and chamber dimensions (V and h) are all measured. Kaplan et al. (1988) has devised a method for calculating loss term by calculating the slope of the plot of $-\ln\left[\frac{C_{eq} - C(t)}{C_{eq} - C_o}\right]$ versus time (t). For this experiment, C_o is the initial equilibrium state H_2S concentration measured by the chamber system at a constant flow rate (lpm). C_{eq} is the measured H_2S concentration at a second equilibrium state at an increased or reduced flow rate into the chamber system (~5-6 lpm difference). $C(t)$ depicts H_2S concentration at any time, t , during the transition between the first and second equilibrium states. L is determined by:

$$L = \left(slope - \frac{q}{V} \right) \left(\frac{V}{A_w} \right) \quad (11)$$

1.2.5 Instrumentation/Theory of Operation

The Model 450C is based on the principle that H_2S can be converted to SO_2 . SO_2 molecules absorb ultraviolet (UV) light and become excited at one wavelength, and then decay to a lower energy state emitting UV light at a different wavelength. Specifically,

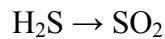


Figure 1.10 shows a schematic of the functional components of the Model 450C analyzer.

The sample is drawn into the Model 450C through the sample bulkhead. From the bulkhead it is either shunted to a converter or bypasses the converter and is led straight through to a hydrocarbon kicker. If the sample passes through the converter H_2S levels can be inferred. If SO_2 readings are required, the sample is not passed through the

converter. The kicker removes hydrocarbons from the sample by forcing the hydrocarbon molecules to differentially permeate through the tube wall. As the sample flows into the fluorescence chamber, pulsating UV light excites the SO₂ molecules.

As the excited SO₂ molecules decay to lower energy states, they release UV light that is proportional to the SO₂ concentration. The UV light emission is detected by a photo multiplier tube (PMT). This detector, located at the back of the fluorescence chamber, continuously monitors the pulsating UV light source and is connected to electronic circuitry that compensates for fluctuations in UV light. The Model 450C outputs the SO₂, H₂S, and CS (complete sulfur) concentration to the front display panel as well as the analog outputs (obtained from TEI Model 450C Instruction Manual, Franklin, MA).

The manufacturer specifies that the lower detectable limit is 1.0 ppb for a 60 second averaging time, above which mean concentrations can be resolved for estimation of H₂S fluxes.

1.2.6 Calibration

A multi-point calibration for the Model 450C analyzer was conducted prior to each sampling campaign using a TEI Model 146 dilution-titration system in conjunction with cylinders of 0.5 ppm of SO₂ in nitrogen (80% of full-range scale) and 0.5 ppm of H₂S in nitrogen (80, 60, 40, and 20% of full-range scale) (Machine and Welding Purity Gases, NIST certified). The TEI Model 146 was serviced and calibrated to specification by the manufacturer and was recertified by North Carolina Division of Air Quality (NC DAQ) technicians. During the field study, zero and span checks for H₂S concentration

(80, 60, 40, and 20% of full-range scale) were conducted daily according to the TEI Model 450C Instruction Manual (Franklin, MA).

1.2.7 Meteorological and Lagoon Parameters Instrumentation

A 10 meter meteorological tower was erected to measure the following meteorological parameters: wind speed and direction, air temperature, relative humidity, and solar radiation (Figure 4.9). A Met One Instruments Model 034-B Windset (Campbell Scientific, Inc., Logan, UT) with an integrated cup anemometer and wind vane mounted on a common shaft was used to measure wind speed and direction at 10 m above the surface. Accuracy of the measured wind speed component is $\pm 0.12 \text{ m s}^{-1}$ for wind speeds below 10.1 m s^{-1} and $\pm 1.1\%$ of reading for wind speeds above 10.1 m s^{-1} . The wind direction component has an accuracy of $\pm 4^\circ$ and a threshold of 0.4 m s^{-1} . Air temperature and relative humidity (RH) measurements was made at 2 m height with a Model CS500-L Vaisala 50Y temperature and RH probe (Campbell Scientific, Inc., Logan, UT) housed in a Model 41303 RM Young 6-plate gill solar radiation shield (Campbell Scientific, Inc., Logan, UT). Accuracy is $\pm 3\%$ over 10-90% RH and $\pm 6\%$ over 90-100% RH while air temperature accuracy is 0.2 to 0.5°C. Solar radiation measurements were made at 2 meter height (facing south) using a Model LI200X Silicon Pyranometer fixed calibration probe (Campbell Scientific, Inc., Logan, UT). Solar radiation has an absolute error in natural daylight of 5% maximum and 3% typical, and a sensitivity of $0.2 \text{ kW m}^{-2} \text{ mV}^{-1}$.

A Model CSIM11 pH probe (Campbell Scientific Inc., Logan, UT) accuracy of $\pm 0.1\%$ over full range continuously monitored lagoon pH during measurement periods. The pH probe was periodically buffer tested to ensure accuracy and calibration curves

were established. Two CS107 (Campbell Scientific Inc., Logan, UT) temperature probes with an accuracy of ± 0.4 °C simultaneously measured lagoon temperatures both inside the chamber and 0.3 m outside the chamber to ensure there were no significant differences between the locations. These pH and temperature probes were submerged in the lagoon at a depth of ~ 15 cm. Data was collected every second, and averaged and recorded over a 15 minute timeframe. Lagoon water samples were collected 1-2 times per day (morning and afternoon) from the measurement location and at one other random location from the lagoon and submitted to the North Carolina Division of Water Quality for total sulfide analysis.

1.2.8 Data Acquisition System and Mobile Laboratory

A Dell Inspiron 600m laptop computer and a Model CR10X Data logger equipped with a Model AM 16/32 Channel Relay Multiplexer (Campbell Scientific, Inc., Logan, UT) was used as an automated data acquisition system. The CR10X data logger recorded 15-minute averaged measurements for H_2S concentrations inside the chamber, lagoon pH, and lagoon temperature. From a 10 meter tower, the CR10X also collected 15-minute averaged measurements of meteorological parameters, i.e., wind speed and direction, solar radiation, temperature, and relative humidity. The 15-minute-averaged H_2S concentrations in the chamber were used to calculate H_2S flux during data analysis. Recorded values were checked periodically against the display panel of detection instruments to ensure accuracy.

The pulsed fluorescence $\text{H}_2\text{S}/\text{SO}_2$ analyzer and NH_3 analyzer was housed in a temperature-controlled mobile laboratory (N.C. State University Air Quality Ford

Aerostar Mini-Van shown in Figure 1.8). The temperature inside the van was monitored and maintained at $\sim 21^{\circ}\text{C}$ ($\sim 70^{\circ}\text{F}$).

1.3 Objectives

The primary objectives of this research initiative were:

- 1.** Design a field study to measure hydrogen sulfide emissions from various source areas including anaerobic waste storage lagoons and confined animal housing buildings, at a commercial swine facility.
- 2.** Investigate and evaluate the variability of these emissions with respect to diurnal and seasonal variations as well as the influence of meteorological and physico-chemical factors.
- 3.** Model the transport of hydrogen sulfide from an anaerobic swine lagoon system based on gas-liquid transport theory under different conditions in both gas and liquid phases.
- 4.** Compare and contrast model results with field measurements made using a dynamic flow-through flux chamber.

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Table 1.1. Fluxes of the global atmospheric sulfur cycle [obtained from Aneja (1990)]

	Junge (1963)	Robinson and Robbins (1968)	Kellog <i>et al.</i> (1972)	Friend (1973)	Moller (1984)	Smil (1985)	Warneck (1988)
Emission source or sink	Fluxes (Tg-S yr⁻¹)^a						
Gaseous emissions							
Anthropogenic Emissions	40	73	50	65	75	98(82-112)	103 ^c
Biogenic Emissions, total	230	98	90	106	70	140(70-175)	43
From oceans	160	30 ^b	-	48 ^b	35	75(40-95)	36
From soils	70	68	-	58	35	65(30-80)	7
Volcanic Gases	-	-	1.5	2	2	10(5-30)	7
Particulate sulfate emissions							
Seaspray	44	44	44	44	175	45(40-60)	150
Mineral dust	-	-	-	-	-	-	?
Anthropogenic SO ₄ ²⁻	-	-	-	-	-	-	3
Wet and dry deposition							
SO ₂ over the oceans	70	25	^d	25			15
SO ₂ over the continents	70	26	15	15	30		71
Excess SO ₄ ²⁻ over oceans		31	29	31			28
Excess SO ₄ ²⁻ onto continents	70	90	96	102			42
Seasalt over oceans	60 ^b	40	44	40	157		135
Seasalt onto continents		4	-	4	18		15
Sum of fluxes							
Total budget	270	215	185	217	322	293(197-377)	306
Flux from continent to ocean	-	26	-	8	-		11
Flux from ocean to continent	-	4	-	4	-		18

^a 1 Tg = 10¹²g^b Junge calculated excess sulfate^c Includes 3(1-5) Tg S yr⁻¹ of reduced sulfur^d Included in excess SO₄²⁻

Table 1.2. Natural Sources of Sulfur in the Atmosphere (Gmol year⁻¹ of sulfur).
[Source: Warneck (2000)]

Source	H ₂ S	DMS	CS ₂	COS
Oceans	<9	500-1300	2.4-9.5	2.8-7.8
Coastal Wetlands	0.2-30	0.2-18	0.2-1.2	2.3-8.7
Soils and Plants	2-56	3-24	0.4	-
Volcanoes	16-47	-	0.2-2.4	-
Biomass Burning	-	-	-	0.7-4.3
CS₂ and DMS Oxidation	-	-	-	4.5-14.8
Total	18-133	503-1342	3.3-14.1	10.4-37.1

Table 1.3. List of reduced sulfur compounds targeted for analysis in this study and their corresponding odor thresholds

Compound	CAS*	Chemical Formula	Odor Detection Threshold (ppb)†	Sensory & Odor Characteristics‡
Carbon disulfide	75-15-0	CS ₂	11 - 32	
Carbonyl sulfide	463-58-1	COS	102	
Dimethyl disulfide	624-92-0	CH ₃ SSCH ₃	0.29 - 12	Putrid, garlic
Dimethyl sulfide	75-18-3	CH ₃ SCH ₃	0.12 – 63.23	Stench, decay
Ethyl mercaptan	75-08-1	C ₂ H ₅ SH	0.017 – 0.7	Onion-like odor
Hydrogen sulfide	7783-06-4	H ₂ S	0.07-195	Rotten eggs
Methyl mercaptan	74-93-1	CH ₃ SH	0.0002-19.4	Rotten cabbage

* Chemical Abstract Service registry number

† Obtained from Clanton and Schmidt (2000)

‡ Merck Index

Table 1.4. Lifetimes at room temperature for the reactions of OH and NO₃ radicals with some reduced sulfur compounds. [Source: Warneck (2000)]

Compound	OH (day)	NO ₃ (night)
COS	63 yr	-
CS ₂	8 days	-
H ₂ S	5 days	-
CH ₃ SCH ₃	4 days	1.1 hr
CH ₃ SH	17 hr	1.1 hr
CH ₃ SSCH ₃	2.8 hr	26 hr

Table 1.5. Observed mixing ratios and emissions of reduced organic sulfur compounds from various studies.

	Heber <i>et al.</i> (1997)	Yang <i>et al.</i> (1998)	Zhu <i>et al.</i> (2000)	Ni <i>et al.</i> (2002)
Ambient Conditions	January-March	Annual	September	Summer (mean daily average)
Measurement Technique	Unknown	Chamber system; Turbidmetrically after dry ashing	Collection: Tedlar™ bag Analysis: Sensidyne detector tubes	SO ₂ analyzer with thermal oxidizer
Measurement Location	Naturally ventilated swine finishing building	Rice Paddies with hog manure applied, Xiaolingwei, Nanjing, China	Mechanically and naturally ventilated swine finishing buildings	Mechanically ventilated swine finishing building
Observed Concentration Hydrogen Sulfide (ppb)	221		414 (NV) ^d 271 (MV) ^e	173 ± 21
Observed Emissions Hydrogen Sulfide	0.90 g day ⁻¹ ^a	0.08 µg-S g ⁻¹ soil (CF) ^b 0.0 µg-S g ⁻¹ soil (CF, OM) ^c	2.00 g day ⁻¹ (NV) ^{a, d} 3.32 g day ⁻¹ (MV) ^{a, c}	578 ± 55 g day ⁻¹ ^f or 8.3 ± 1.1 g day ⁻¹ ^a

^a Normalized per 500 kg animal units (AU)

^b Chemical fertilizer applied to soil

^c Chemical fertilizer and organic hog manure applied to soil

^d Naturally ventilated

^e Mechanically ventilated

^f Entire building

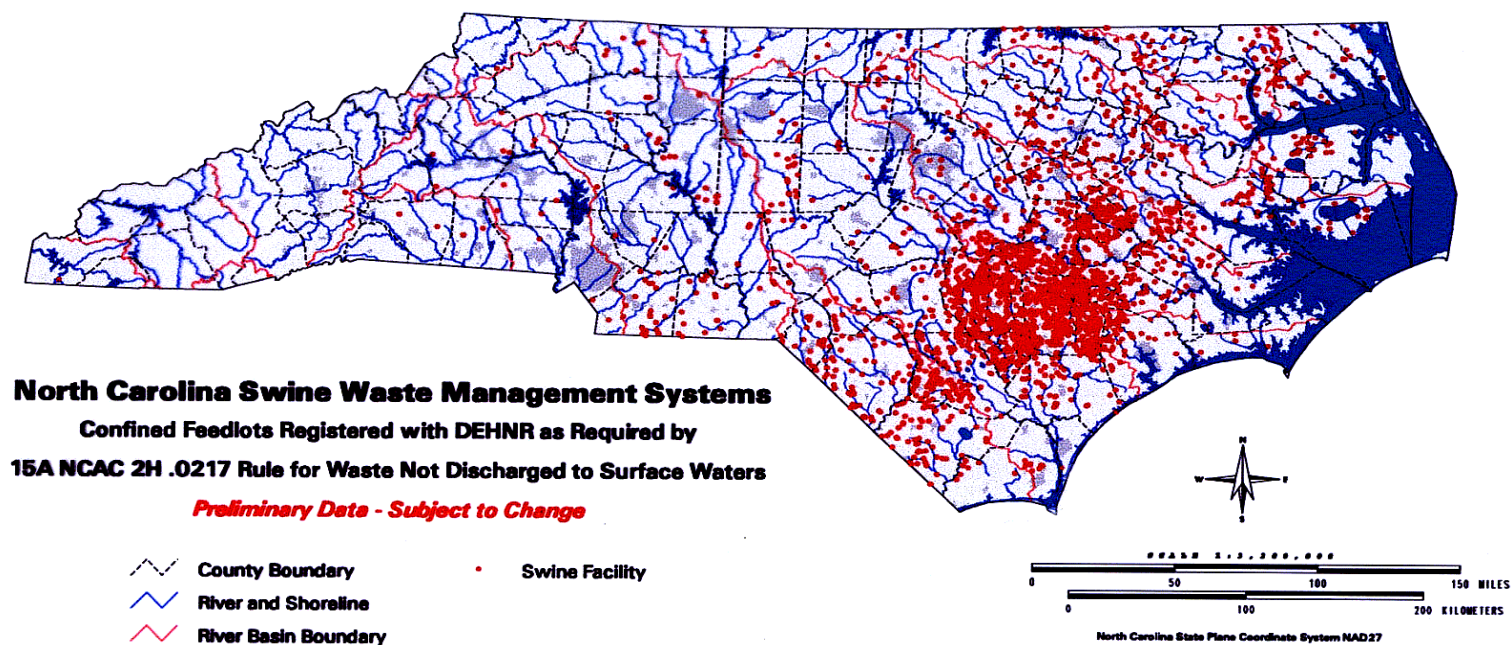
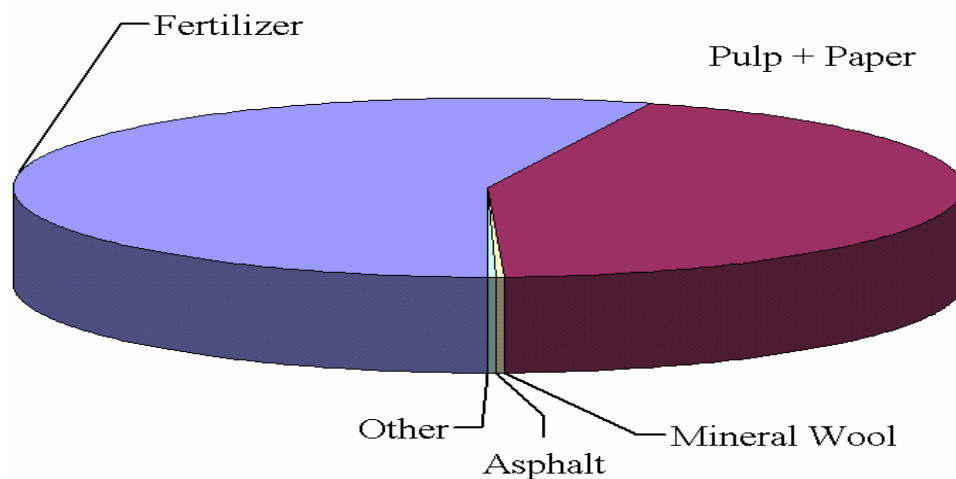


Figure 1.1. North Carolina Swine Facility Locations

Total = 11.9 Million lb H₂S/yr



Industries	2002 Inventory (lb)	
Fertilizer	6,617,304	56%
Pulp + Paper	5,226,227	44%
Mineral Wool	51,562	0%
Asphalt	7,044	0%
Other	12,621	0%

Figure 1.2. North Carolina Division of Air Quality 2002 hydrogen sulfide emissions inventory.
[Source: <http://daq.state.nc.us/toxics/studies/H2S>]

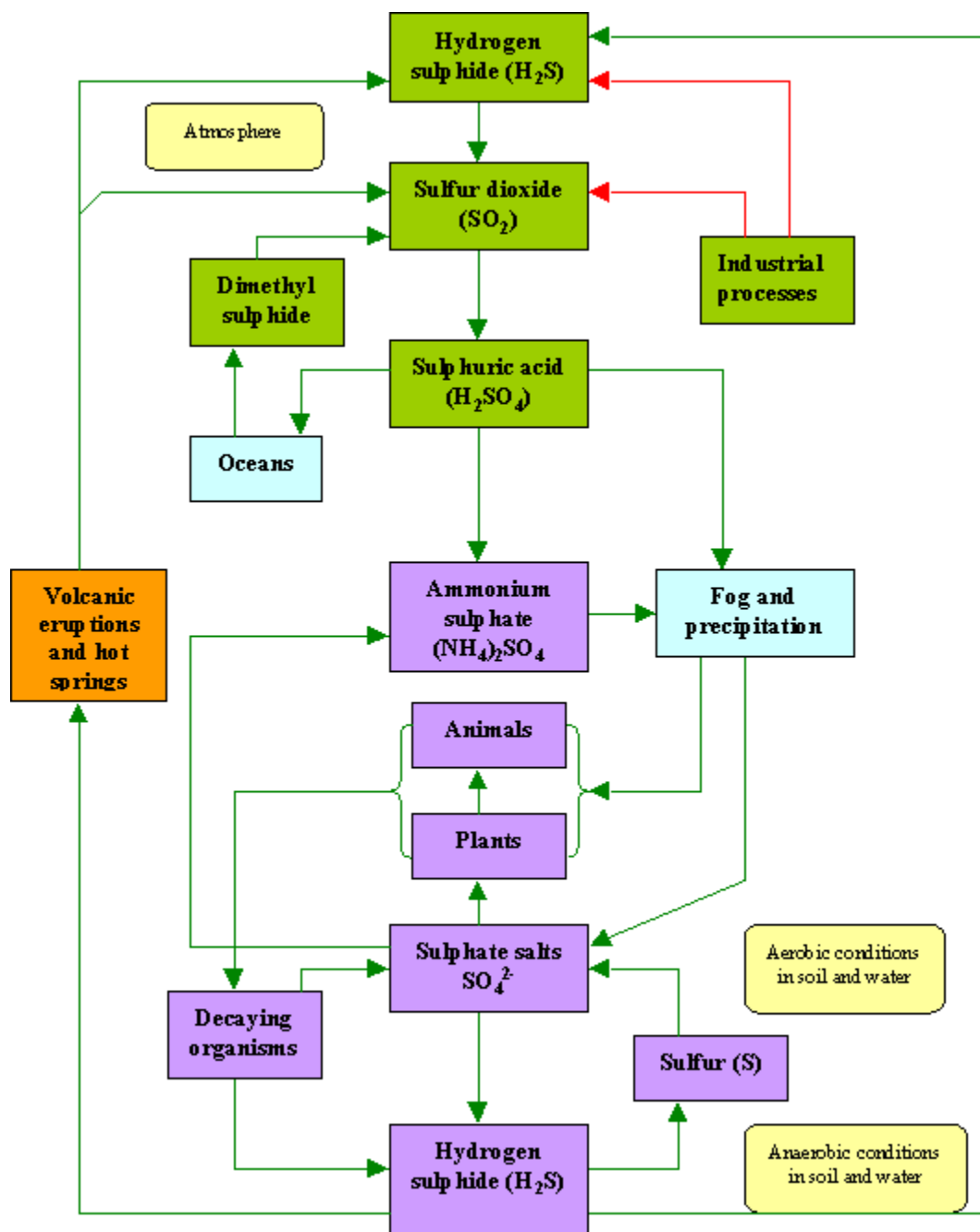


Figure 1.3. Schematic representation of the sulfur cycle.
 [Source: <http://www.lenntech.com/sulfur-cycle.htm>]

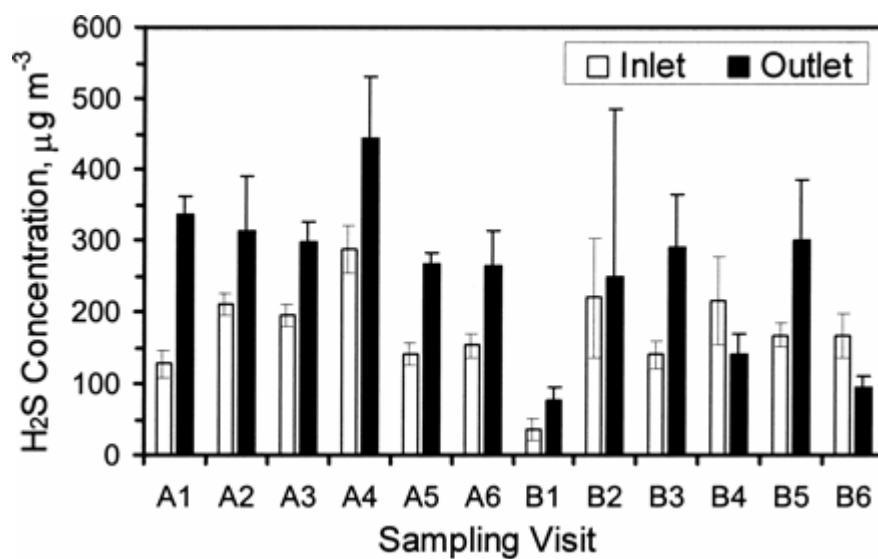


Figure 1.4. Mean buoyant convective flux chamber (BCFC) outlet concentrations of hydrogen sulfide from two anaerobic storage lagoons. [Source: Lim *et al.* (2003)]

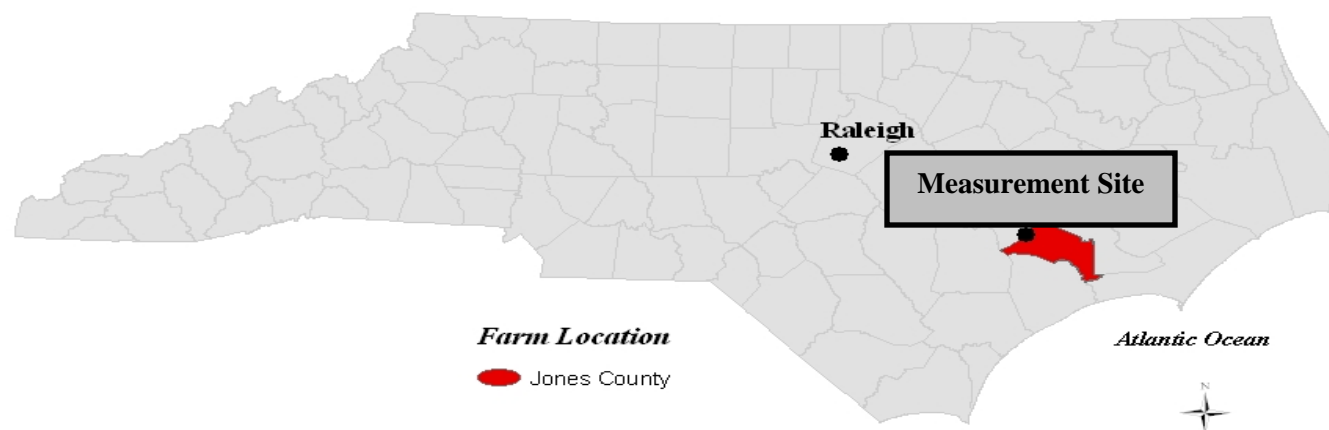
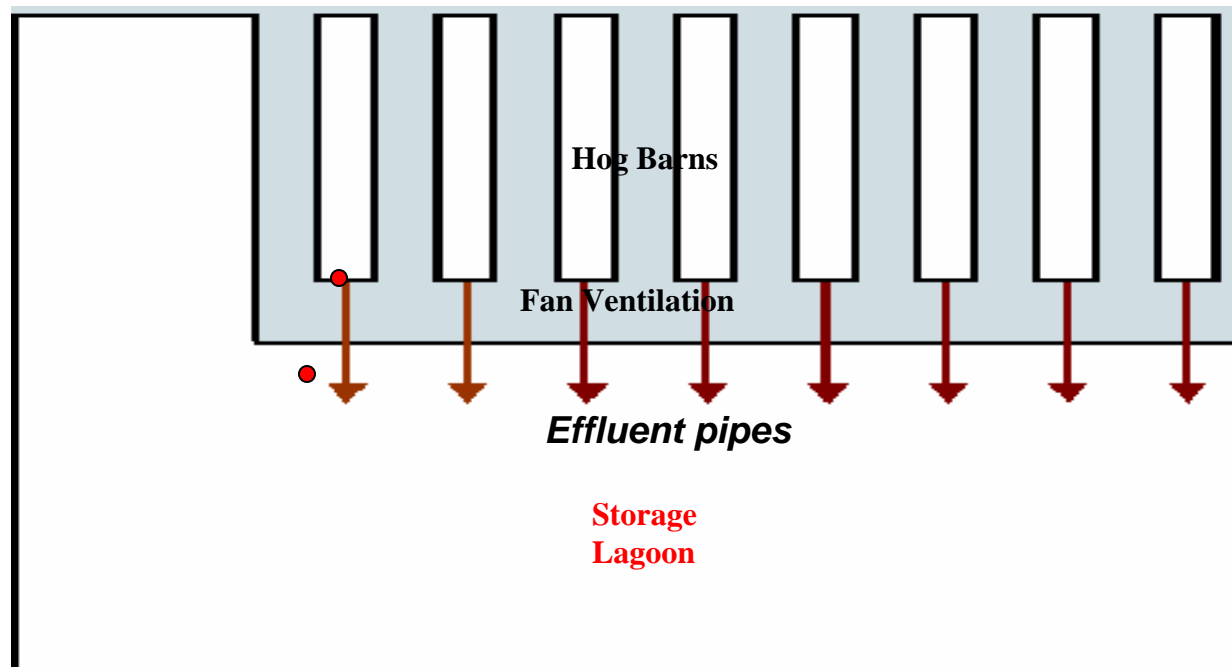


Figure 1.5. Physiographic location of Experimental Site



● Sampling location

Figure 1.6. Schematic of Experimental Site: Lagoon & Spray Technology



Figure 1.7. Dynamic Flow-Through Chamber System.

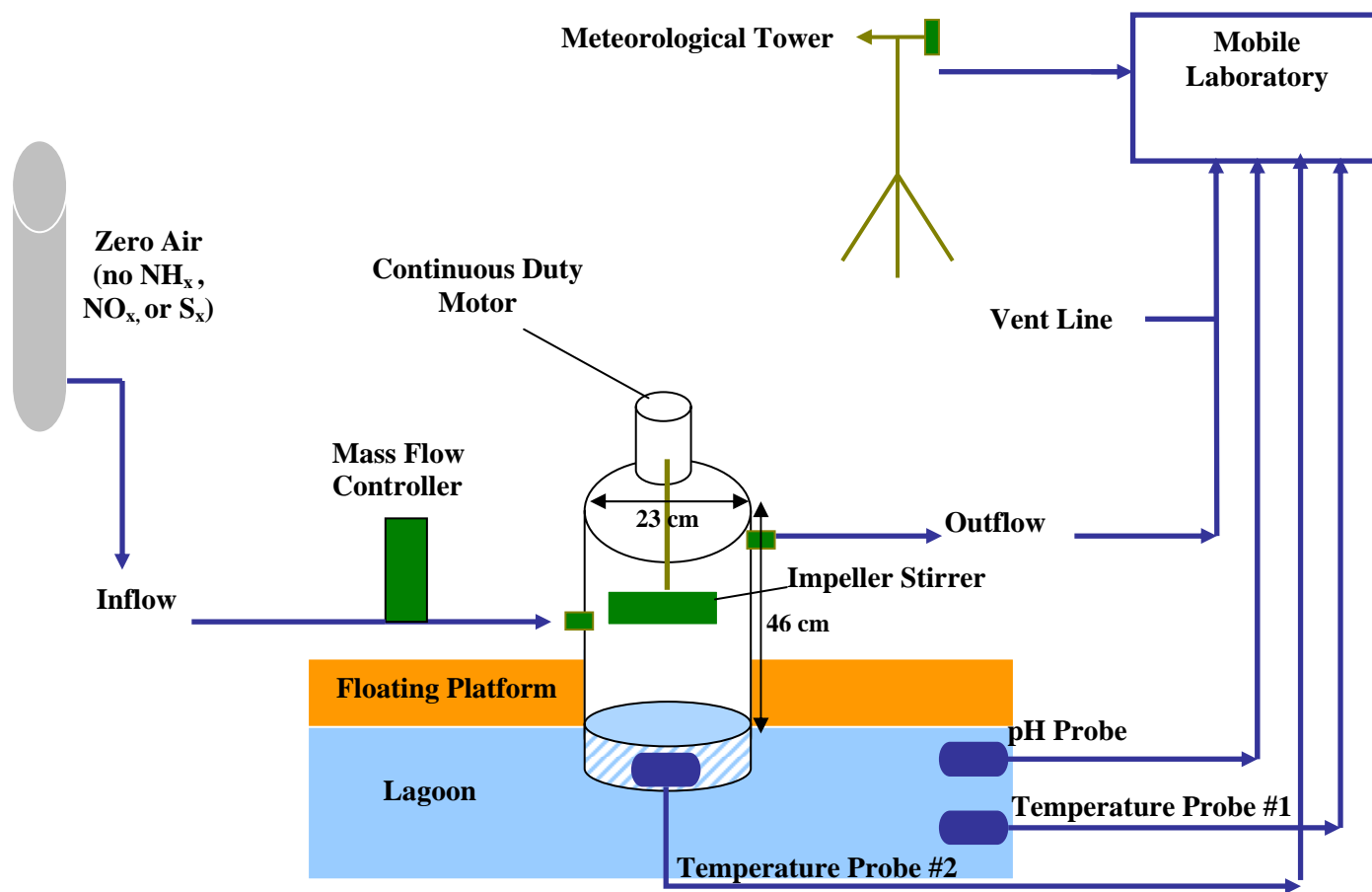


Figure 1.8. Schematic of dynamic flow-through chamber system configured to measure emissions from a swine waste treatment lagoon.

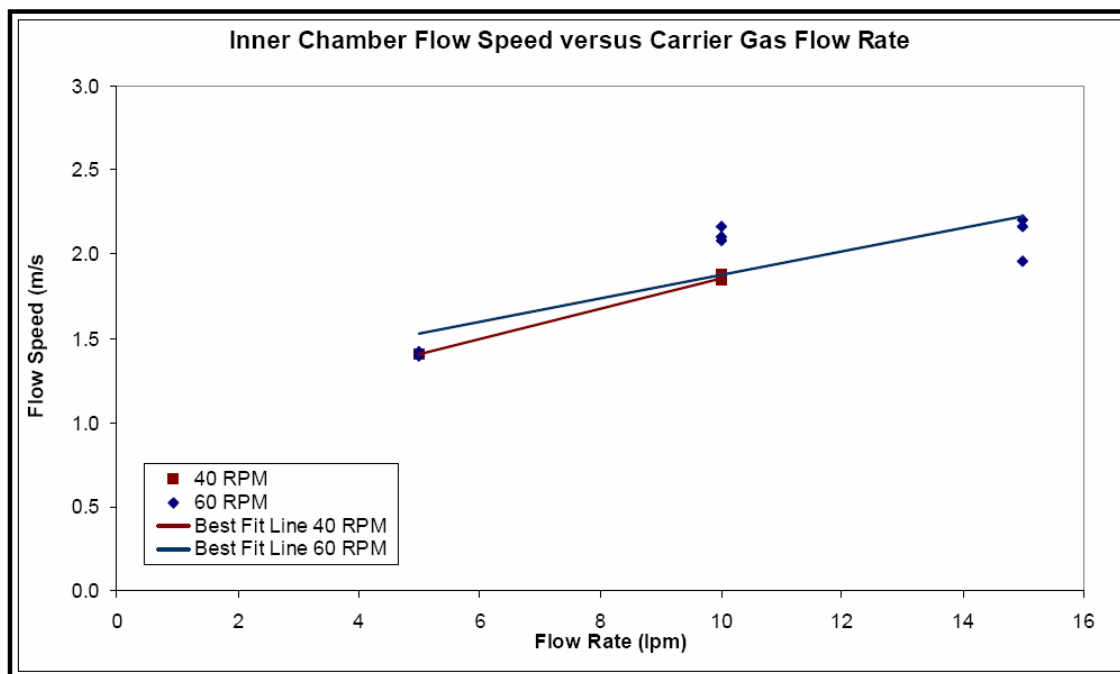
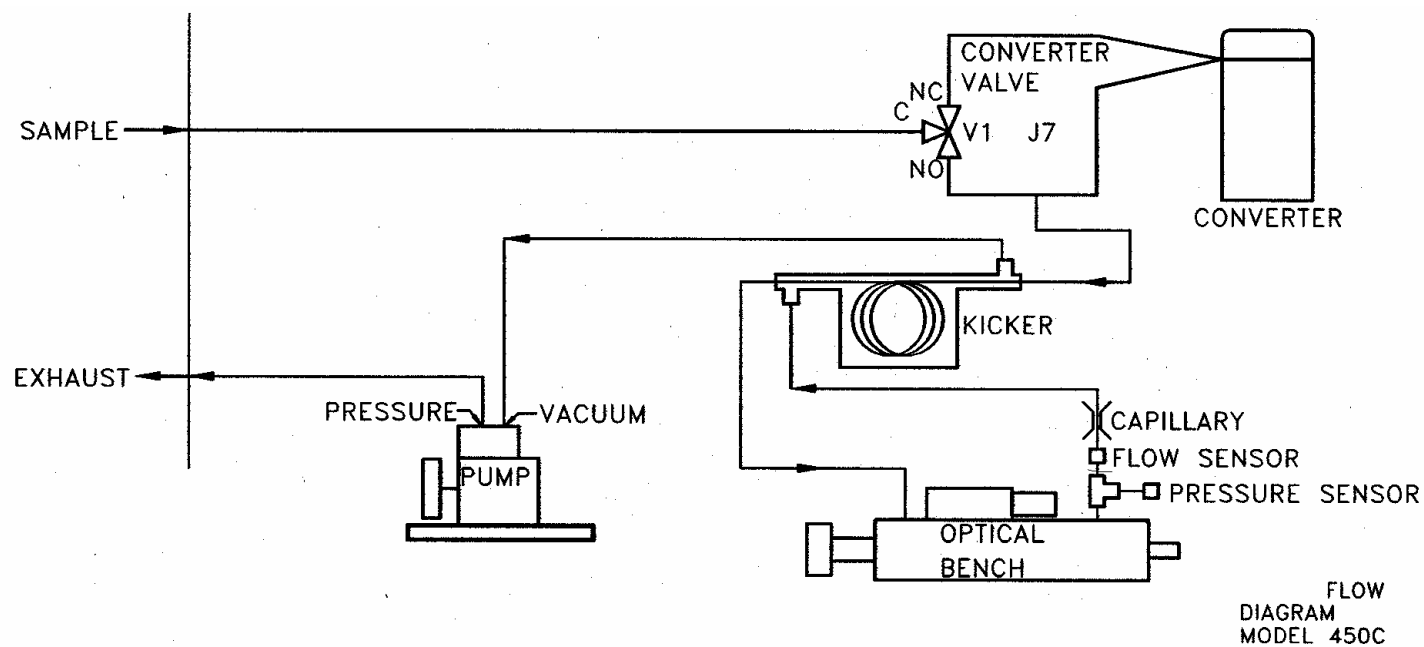


Figure 1.9. Chamber Wind Speed and Carrier Gas Flow Rate. Flow speed indicates the wind speed inside the chamber, referred to as chamber wind speed, measured at ~0.5 m above the lagoon surface. [Source: Arkinson, (2003)]



450P809

Figure 1.10. Schematic of Thermo Environmental Instruments (TEI) Model 450C Pulsed Fluorescence Hydrogen Sulfide Analyzer [Source: TEI, 2002]

CHAPTER II. MEASUREMENT AND ANALYSIS OF AMMONIA AND HYDROGEN SULFIDE EMISSIONS FROM A MECHANICALLY VENTILATED SWINE CONFINEMENT BUILDING IN NORTH CAROLINA

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Abstract

Emissions of atmospheric ammonia-nitrogen ($\text{NH}_3\text{-N}$, where $\text{NH}_3\text{-N} = (14/17)\text{NH}_3$) and hydrogen sulfide (H_2S) from a finishing swine confinement house at a commercial hog farm in eastern North Carolina were measured over a one year period. Continuous simultaneous $\text{NH}_3\text{-N}$ and H_2S emissions were made for ~ 1 week period during four seasons. The number of hogs contained in the house varied from ~ 850 - 900 with average weights ranging from ~ 38 - 88 kg. Average $\text{NH}_3\text{-N}$ concentrations were highest during the winter and spring sampling periods, 8.91 ± 4.61 and 8.44 ± 2.40 ppm, respectively, and lower during the summer and fall, 2.45 ± 1.14 and 4.27 ± 0.71 ppm, respectively. Measured average H_2S concentrations were 673 ± 282 , 429 ± 223 , 47 ± 18 , and 304 ± 88 ppb during winter, spring, summer, and fall, respectively. Generally, the H_2S concentrations were approximately an order of magnitude less than $\text{NH}_3\text{-N}$ during winter, spring, and fall, and two orders of magnitude smaller during the summer season.

The average ambient temperature ranged from 5.5 - 22.3°C while the average barn temperature measured at the outlet fans ranged from 19.0 - 26.0°C in the winter and summer, respectively. The average fan ventilation rates varied from $253 \text{ m}^3 \text{ min}^{-1}$ during the fall sampling period to $1024 \text{ m}^3 \text{ min}^{-1}$ during summer.

Calculated total emission rates for both $\text{NH}_3\text{-N}$ and H_2S were highest during the spring, $4519 \pm 1639 \text{ g-N day}^{-1}$ and $481 \pm 142 \text{ g day}^{-1}$, respectively. Emissions were lowest during the fall season for $\text{NH}_3\text{-N}$ ($904 \pm 568 \text{ g-N day}^{-1}$) and the summer season for H_2S ($82 \pm 49 \text{ g day}^{-1}$). Normalized $\text{NH}_3\text{-N}$ emission rates were highest in winter and spring (33.6 ± 21.9 and $30.6 \pm 11.1 \text{ g-N day}^{-1} \text{ AU}^{-1}$ where $1 \text{ AU (animal unit)} = 500 \text{ kg}$) and lowest during summer and fall (24.3 ± 12.4 and $11.8 \pm 7.4 \text{ g-N day}^{-1} \text{ AU}^{-1}$).

Normalized H₂S emissions were highest during the winter and spring seasons (4.2 ± 2.1 and 3.3 ± 1.0 g day⁻¹ AU⁻¹) and were lowest in summer and fall (1.2 ± 0.7 and 1.7 ± 0.5 g day⁻¹ AU⁻¹).

2.1 Introduction

Changes in livestock production methods in the U.S. are in turn changing emissions of trace gases (e.g., sulfur, carbon, and nitrogen species) into the atmosphere (Aneja et al., 2006). Large-scale commercial operations have emerged over the last few years, dramatically increasing the number of hogs in geographically concentrated areas. In North Carolina, for example, the swine industry has grown significantly since the early 1990s, with an increase in inventory from 2.5 million to 9.8 million animals (Aneja et al., 2001). As the hog population increased over time, the number of hog operations decreased in parallel, from 18 000 in 1985 to 2400 by 2005. The shift in the hog farming industry over the past two decades is illustrated in Figure 2.1. [The hog growth ceased in 1997, due to a moratorium imposed on any new or existing hog farms in the state by the North Carolina State Legislator (House Bill 515; S.L.1997-458)]. Currently, there are more than 1400 operations with more than 1000 head, accounting for almost 99% of the state inventory (<http://www.nass.usda.gov/QuickStats/>), with the vast majority of the hog farms in North Carolina clustered in the southeastern coastal plain region of the state.

Subsequently, emissions of potentially harmful gases such as ammonia, (NH_3) and hydrogen sulfide (H_2S) from confined animal feeding operations (CAFOs) have become a major concern in recent years (Aneja et al., 2001). Public concerns about potential environmental and health effects of air emissions from CAFOs have increased along with the growth and consolidation of this industry.

Ammonia is a byproduct of microbial decomposition of the organic compounds in manure and nitrogen occurs as both unabsorbed nutrients in manure and as urea in urine (U.S. EPA, 2001). Ammonia released from near-surface sources (i.e. confinement

houses and waste treatment lagoons) into the atmosphere generally has a relatively short lifetime of ~1-5 days (Warneck, 2000) and may deposit near the source through dry or wet deposition processes. However, ammonia can also participate in atmospheric reactions (e.g. gas-to-particle conversion) once airborne, forming ammonium aerosols such as ammonium sulfate, -nitrate, -chloride, which tend to have longer atmospheric residence lifetimes (~1-15 days) due to a decrease in dry deposition velocity (Aneja et al., 1998) and therefore may be transported and deposited further downwind from the source. An environmental hazard in eastern North Carolina that has been associated with ammonium aerosols is deposition into sensitive coastal river systems where nitrogen loading may lead to enhanced eutrophication and soil acidification, which may in turn upset plant nutrient balances near sources (Paerl, 1997).

Hydrogen sulfide is a colorless, potentially harmful gas released from swine manure (U.S.EPA, 2003). It is produced as manure decomposes anaerobically, resulting from the mineralization of organic sulfur compounds as well as the reduction of oxidized inorganic sulfur compounds such as sulfate by sulfur-reducing bacteria (U.S. EPA, 2001). The U.S. Center for Disease Control (CDC) warns that brief exposures to concentrations greater than 500 ppm can cause unconsciousness or death and lower levels in the range of 250-500 ppm have been associated with pulmonary edema (ATSDR, 2004). Donham et al. (1982) reported that hydrogen sulfide appeared to be the main toxic substance in liquid manure associated with death and illness for people with acute exposure to gases emanating from liquid manure. Campagna et al. (2004) have reported a correlation between elevated ambient H₂S concentrations and hospital visits for respiratory diseases. 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. However, it is noted that H_2S is just one component of many odorous gases that have been identified in hog farm emissions. Potential negative health effects of overall emissions from hog farms have been identified in production workers and neighboring residents that include respiratory illnesses such as bronchitis and asthma, and increased psychological stress (Schiffman, 1998).

Hoff et al. (2004) reviewed various ventilation measurement methodologies to estimate emission rates from mechanically ventilated CAFOs and Arogo et al. (2003) reviewed several studies, both in Europe and the U.S., undertaken to estimate NH_3 emissions from animal confinement houses. Emissions of ammonia (Zhu et al., 2000; Heber et al., 2000; Schmidt et al., 2002; Jacobson et al., 2005) and hydrogen sulfide (Heber et al., 1997; Zhu et al., 2000; Ni et al., 2002; Schmidt et al., 2002; Jacobson et al., 2005) from swine confinement houses in the Midwestern U.S. have been estimated. It is noted that none of the studies were conducted on farms in the Southeastern U.S. Various factors, such as farming activities (i.e., feed composition, animal density) and regional climates, may affect the emissions of gases into the atmosphere. Emissions estimates generated for one set of conditions or for one type of CAFO may not translate readily to others. It is therefore important for comprehensive emissions measurements to be made from different types of operations in order for accurate emission factors to be estimated.

The primary objective of this research initiative was to investigate and evaluate the variability of ammonia and hydrogen sulfide emissions with respect to diurnal and seasonal variations as well as the influence of meteorological factors on the emission processes. Data presented here was collected continuously for a one-week period during

each season (i.e., fall, winter, spring, summer) for one year from a finishing swine confinement house at a commercial hog farm in eastern North Carolina.

2.2 Methods and Materials

2.2.1 Physiographic Location and Farm Description

The experimental site is an operational commercial swine finishing farm located in Jones County, NC in the southeastern coastal plain region of the state, where the majority of hog farming operations are located. The on-site waste storage treatment lagoon is 3.063 ha (30,630 m²) and the farm maintains eight fan-ventilated confinement houses, aligned North-South and oriented East-West, with each barn measuring 61 x 12.2 meters. Generally, the hogs are rotated out of each house approximately every 18 weeks, weighing ~22-24 kg upon arrival and gaining an average of 5 kg per week. The weight gain is assumed to be linear and the weekly animal mortality rate was documented and taken into account for total weight estimations. Each house is cleaned and sanitized between rotations. There are 800-900 animals housed in each barn and rotations are staggered for each house. The hogs are placed in the barns approximately one week apart, starting with the barn located at the South end. A full description of the hog numbers, weights, and number of weeks in rotation for each season during the initiative is provided in Table 2.1. Each barn has a shallow manure collection pit which is emptied once a week. The farm utilizes a conventional “lagoon and spray” technology as its primary means of handling effluent. The pits are recharged with lagoon liquid that has a total ammoniacal nitrogen (TAN) content of 360 to 590 mg L⁻¹ and a total sulfide content of 0.1 to 13.0 mg L⁻¹ (range is based on samples collected from the lagoon during all four experimental periods). Effluent is flushed directly from the hog barns into the

storage lagoon where it is treated via natural microbial processes. The stored wastewater is used to recharge the barn pits, and also periodically irrigated over on-site agricultural crops for nutrient enrichment purposes.

2.2.2 Experimental Procedure

One barn, located furthest north on the property, was selected for measurements. Five AAA Associates Inc. Maxi-Brute™ fans with plastic shutters (Niles, MI), two 91 cm diameter direct-driven and three 122 cm diameter belt-driven, were located at the west end of the building (see Figure 2.2). The fans were staged to operate as temperature increased inside the building.

In order to determine fan rpms, a Mabuchi VDC motor (Santa Clara, CA) was either (1) mounted to a stainless-steel plate configured to fit over the front of the 91 cm fan plate or (2) attached to a cylinder sleeve which fit over the fan shaft of the 122 cm fans. Single analog output wires were connected from each motor to a Campbell Scientific CR10X data logger (Logan, UT) which continuously recorded the measured voltage output every second and averaged the data over a fifteen minute timeframe. Prior to the experiment, each motor was calibrated in the laboratory to obtain voltage outputs at a specific rpm. For this process, each VDC motor was attached to the shaft of a Dayton SCR Controlled DC Motor (Model # 2M168C). A Shimpo DT-725 Stroboscopic Digital Tachometer and Shimpo DT-207B Direct Contact Digital Tachometer (Itasca, IL) were used to determine revolutions per minute (rpm) and a Micronta Digital Multimeter (Model # 22-185) was used to simultaneously determine voltage output at the respective rpm. Figure 2.3 shows the linear conversion of voltage to rpm. The rpm for each fan as well as “on/off” times could then be determined and flow rates subsequently calculated.

According to manufacturer specifications the direct drive motor on the 91 cm fans is rated at 850 rpm and the 122 cm fan motor is rated at 1725 rpm. We estimated the “pulley ratio” for the 122 cm fans to be 2.9:1; therefore, the fans should be rotating at ~595 rpms. However, fan belts may become loose over time and the rpms decrease, thus affecting the flow rate. Broken shutters and excess dirt on fan blades may also reduce air flow rates through the exhaust systems. Janni et al. (2005) conducted a study to test fan flow rates and found that 122 cm diameter belt-driven fans with 1-hp motor and plastic shutters was 58-65% of laboratory airflow rate (Bioenvironmental Engineering Structure Systems (BESS) Lab, University of Illinois at Urbana-Champaign) and that fans with loose belts had airflow rates that were 72-74% of fans with tight belts.

The static pressure inside the building was monitored during the spring season using a Model PX655 Omega pressure transducer to measure the pressure difference between the inside of the barn (placed away from any wind currents) and the outside ambient air (tubing housed inside the mobile laboratory). The pressure sensor did not work properly during the other seasons. However, during the spring initiative the full range of ventilation rates was recorded (i.e., all five fans turned on at some point) and the static pressure was found to vary from 0.22 – 0.32 cm water (21 – 31 Pa), with an average and median value of 0.28 cm water. This value was subsequently used for further emission rate calculations. The flow rates for each fan size were calculated using the following calculation

$$CalculatedFlowRate = \left(\frac{ManufacturerFanFlowRate}{SpecifiedRPMs} \right) (MeasuredRPMs) \quad (1)$$

where the manufacturer fan flow rate was adjusted to the average static pressure measurements. For example, given a static pressure of 0.28 cm water, manufacturer fan

flow rates for the 91 cm fan with shutter and 122 cm fan are ~ 269 and $\sim 640 \text{ m}^3 \text{ min}^{-1}$, respectively.

A $\frac{1}{4}$ " o.d., $\frac{5}{32}$ " i.d. Teflon sample line was inserted inside the chimney of the first 91 cm fan to turn on, between the shutter and fan blade, at roughly half the fan radial distance (see Figure 2.2). Due to the nature of the airflow through the building, it is assumed that the gaseous concentrations are uniformly distributed at each fan outlet. The air is drawn through the system and is then split using a Swagelok® stainless steel Union Tee in order to deliver the sample simultaneously to the different analysis instruments: a Thermo Environmental Instruments (TEI) Model 450C pulsed fluorescence $\text{H}_2\text{S}/\text{SO}_2$ analyzer and a Model 17C chemiluminescence NH_3 analyzer (Thermo Environmental Corporation, Mountain View, CA). The Model 450C analyzer draws in sample air at $\sim 1.0 - 1.2 \text{ L min}^{-1}$ through an internal vacuum pump and the Model 17C analyzer draws in sample air at $\sim 0.5 \text{ L min}^{-1}$ via an external vacuum pump (KNF Neuberger, Inc., Trenton, NJ); therefore the sample entering each analyzer is free of contamination.

Multi-point calibrations (80, 60, 40, and 20% of full-range scale) for the Model 450C and Model 17C analyzers were conducted according to the TEI Model 450C and Model 17C instruction manuals prior to each sampling campaign using a TEI Model 146 dilution-titration system (Thermo Environmental Corporation, Mountain View, CA). During the field study, zero and span checks for H_2S and NH_3 concentration were conducted daily and results added to the calibration curve.

Five-minute integrated background samples were collected daily using an SKC Vac-U-Chamber system and 10-L Tedlar® bags (Fullerton, CA). A vacuum collection box (SKC_West Inc., Fullerton, CA) was used to draw air into the bags, thus allowing air

to enter the collection bag free of any contamination. The sample was drawn through a Teflon tube which was split using a Swagelok® stainless steel Union Tee and delivered to the respective H₂S and NH₃ analyzers (temporarily disconnected from the fan outlet sample line). There was a 5-10 minute gap between the time the barn sample line was disconnected and replaced by the background sample line. Data was recorded from the background samples after three minutes, allowing the instruments to stabilize.

Concentration levels were subsequently recorded from each analyzer. The background samples collected were on average 0-4% of the concentration values measured for both NH₃ and H₂S at the fan ventilation exhaust and were therefore not considered during emission calculations.

Inside the confinement house, the concentration distribution of the gases was assumed to be uniform across the front of the barn where the fans are located. The barn emission rates are therefore calculated by the following equation:

$$J = C * \sum f \quad (2)$$

where C is the measured gas concentration at the fan outlet and $\sum f$ is the sum of the calculated flow rates for each fan.

2.2.3 Meteorological and Data Acquisition Instrumentation

A 10 meter meteorological tower was erected to measure ambient air temperature and relative humidity. Air temperature and relative humidity (RH) measurements were made at 2 m height with a Model CS500-L Vaisala 50Y temperature and RH probe (Campbell Scientific, Inc., Logan, UT) housed in a Model 41303 RM Young 6-plate gill solar radiation shield (Campbell Scientific, Inc., Logan, UT). Additionally, a CS107

temperature probe (Campbell Scientific Inc., Logan, UT) was placed next to the sample line in order to measure the temperature at the fan exhaust.

A Model CR10X data logger equipped with a Model AM 16/32 Channel Relay Multiplexer (Campbell Scientific, Inc., Logan, UT) was used to collect all meteorological, fan voltage, and gas measurement data. A Dell Inspiron 600m laptop computer was used to download the data, which was collected every second, and averaged and recorded over a 15 minute timeframe. The data loggers and gas analyzers were housed inside a temperature-controlled mobile laboratory (N.C. State University Air Quality Ford Aerostar Mini-Van), maintained at $\sim 21^{\circ}\text{C}$ ($\sim 70^{\circ}\text{F}$).

2.3 Results

2.3.1 Ammonia and Hydrogen Sulfide Concentrations

All results for ammonia are presented as ammonia-nitrogen ($\text{NH}_3\text{-N}$). To convert to NH_3 , multiply the value by 1.214. Table 2.2 gives mean seasonal concentration values for $\text{NH}_3\text{-N}$ and H_2S measured at the first 91 cm diameter exhaust fan to turn on in series as well as total fan ventilation rates, temperature measured at the fan exhaust, and ambient temperature and relative humidity measurements. Average $\text{NH}_3\text{-N}$ concentrations were highest during the winter and spring sampling periods, 8.9 and 8.4 ppm, respectively. Maximum values of ~ 14 ppm were measured during both seasons. The higher concentration values during the winter may be attributed to less airflow through the building since the ambient and barn temperatures are generally cooler and the fans are staged to turn on at predetermined temperature set points. A buildup of the gas therefore occurred with fewer fans operating. Although the spring ventilation rates are more than double the rates during the winter time, it is likely that the large concentrations

measured in the spring are due to the age and weights of the animals housed in the barn (see Table 2.1). During the spring, the average hog weight was ~88 kg (see Table 2.1) as compared to 38-58 kg during the other seasons when measurements were made.

The lowest concentrations measured at the fan exhaust occurred during the summer experimental period. At least two 91 cm fans were almost always operational and usually four or five were turned on during the daytime. The buildup of gas inside the barn is minimized because the ventilation rates are continuously higher than during the cooler seasons. Another contributing factor may also be that the animals are in week # 4 of the rotation, weighing an average of 38 kg.

The daily averaged H_2S concentrations were approximately an order of magnitude less than $\text{NH}_3\text{-N}$ during winter, spring, and fall, and two orders of magnitude smaller during the summer season. Similar to $\text{NH}_3\text{-N}$, measured H_2S concentrations were highest during the winter and lowest during the summer, 673 and 47 ppb, respectively. The average H_2S concentration was 6-14 times less during the summer sampling period as opposed to the other seasons.

Since temperature normally increases during the daytime and the fan operating system is temperature dependent, it is expected that the concentration measured at the first staged fan should be highest during the nighttime when fewer fans are running and lower during the daytime when more fans are usually turned on and ventilation rates are higher. Figure 2.4 depicts the hourly averaged diurnal profile for H_2S and $\text{NH}_3\text{-N}$ during each season. The diurnal H_2S concentration patterns generally show a decrease during the early to mid-morning hours and an increase as temperatures begin to fall in the late

afternoon. During the summer, the pattern is less defined during the afternoon and the concentration remains relatively steady during the daytime.

During the winter and fall sampling periods, the $\text{NH}_3\text{-N}$ concentrations actually begin to increase in the mid-morning and continue until early afternoon. Jacobson et al. (2005) measured ammonia at the exhaust of two mechanically ventilated swine buildings and the diurnal profiles for the warm months at a gestation house and cool months at a breeding house also indicated a slight increase in concentration during the midday. Possibly, gas accumulation inside the barn during cooler temperatures (i.e., lower fan flow rate) or animal activity in the barn may affect the emissions; however, it is unclear why this pattern does not also exist for H_2S .

2.3.2 Ammonia and Hydrogen Sulfide Emission Rates

Total and normalized emission rates (500 kg per AU where AU = Animal Unit) for both $\text{NH}_3\text{-N}$ and H_2S are given in Table 2.3. Calculated total emission rates for both $\text{NH}_3\text{-N}$ and H_2S were highest during the spring, 4519 and 481 g day^{-1} , respectively. Emissions were lowest during the fall season for $\text{NH}_3\text{-N}$ (904 g-N day^{-1}) and the summer season for H_2S (82 g day^{-1}).

The average emission rate for each season was further normalized, thus removing the total live mass as a variable to explain emission rates. The normalized value is obtained by dividing the total emission rate by total live mass and then multiplying by 500 kg (1 AU). The normalized emission rates ranged from 11.8-33.6 $\text{g-N day}^{-1} \text{ AU}^{-1}$ for $\text{NH}_3\text{-N}$ and 1.2-4.2 $\text{g day}^{-1} \text{ AU}^{-1}$ for H_2S . The normalized emission rate for H_2S from the barn was ~3.5 times higher during the winter season compared to summer and the

normalized emission rate for $\text{NH}_3\text{-N}$ was almost three times higher in winter than fall, thus indicating that emissions may not increase linearly with animal mass (see Table 2.1).

Normalizing the data provides an effective means to compare emission rates between studies. Table 2.4 and Table 2.5 compare estimated emission rates of $\text{NH}_3\text{-N}$ and H_2S , respectively, from this study with previous studies. Normalized $\text{NH}_3\text{-N}$ emission rates measured during April and June (30.6 and $24.3 \text{ g day}^{-1} \text{ AU}^{-1}$) are higher than rates reported by Lim et al. (2004) from May-July for one week pit recharge ($8.2 \text{ g day}^{-1} \text{ AU}^{-1}$). However, that study was conducted inside a building at the Purdue University Swine Research Center as opposed to an operational farm. Emission rates were lower than Heber et al.(2000) during the summer, June-September (120 and $78 \text{ g day}^{-1} \text{ AU}^{-1}$, measured from two barns). On the other hand, calculated emission rates from this study during the winter sampling period ($33.6 \text{ g day}^{-1} \text{ AU}^{-1}$) are higher than those reported by Schmidt et al. (2002) from a mechanically ventilated barn from February to March ($6.6 \text{ g day}^{-1} \text{ AU}^{-1}$). It is noted that both Heber et al. (2000) and Schmidt et al. (2002) made measurements from barns containing deep pits for manure storage.

The measured normalized emission rates of H_2S compare well with those in the literature; however, Schmidt et al. (2002) reported a much lower rate of $0.0007 \text{ g day}^{-1} \text{ AU}^{-1}$ during the winter. Although normalizing the calculated emissions by the weight of the animals is helpful for comparison, it does not take into account factors such as animal age, length of time in rotation, length of time since the house has been cleaned and/or waste removal, temperatures, and ventilation rates, all of which may also play a role in emissions.

Hourly averaged normalized $\text{NH}_3\text{-N}$ and H_2S emissions were graphed in Figure 2.5 to show the diurnal profiles for each season. It would be expected that the emission rates remain relatively steady throughout the profile since gas concentrations decrease as ventilation rates increase. However, the emission rates for $\text{NH}_3\text{-N}$ increased during the warmer daytime hours and decreased during the night for all seasons. The warmer temperatures during the daytime likely enhance the volatilization of the gas from the animal waste.

The H_2S spring diurnal profile exhibits a slight decrease in emission rates during the late morning to early afternoon while the remainder of the day remains fairly stable. The emission rates increase more dramatically during the daytime in the winter. During two days of the measurements, all fans turned off during much of the overnight hours and emissions were negligible, influencing those nighttime average emission rates.

2.4 Discussion

There are several parameters that may affect gaseous concentrations inside the barns as well as the emission rates via mechanically-ventilated fan exhaust systems, including age and weight of the animals housed inside the barn, waste storage and/or flushing frequency, amount of time since the inside of the barn was cleaned and sanitized, fan ventilations rates, barn temperatures, which influence ventilation rates as well as gas volatilization, and meteorological parameters (i.e., ambient temperature, relative humidity).

The amount of time the animals and/or animal waste have been housed inside the confinement structure may play a large role in the gas emission rates from the barns. In houses with deep pits, the waste may be stored beneath the floor for months and the

normalized emission rates would not necessarily be reflected by the animal weights alone as waste accumulates. Similarly, in a house with shallow pits, although the pits are recharged frequently (i.e., daily or weekly), the houses are only cleaned and sanitized between animal rotations and so a buildup of waste may occur over time as well. For example, during the summer experiment it was roughly one month since the house had been cleaned as opposed to more than three months for the spring sampling period and the normalized emission rates for H₂S were three times higher during the spring season. For this study design, it was not possible to investigate this possible influence and other parameters may certainly have influenced the emissions as well. In a previous study, Lim et al (2004) determined that weekly or bi-weekly pit recharge with recycled secondary lagoon effluent reduced NH₃ and H₂S emissions by 51-62% and 18-40%, respectively, compared to corresponding storage times without pit recharge. Daily flushing was even more effective, reducing NH₃ emissions by 45% and H₂S emissions by 58% compared to the weekly cycles. It should be considered that the concentration of TAN and total sulfide in the recharge may influence barn emission rates.

Pearson's Correlation Coefficients were calculated to examine the individual relationships between total fan flow rates, gas concentrations, normalized gas emission rates, ambient and fan exhaust temperature and ambient relative humidity using a statistical software package (SAS Institute Inc., Cary, NC). The results are presented in Table 2.6. Ventilation fans are used to create airflow in the hog barns in order to remove warm, concentrated air, thereby maintaining relatively steady temperatures and good indoor air quality. It is therefore expected that concentration levels will decrease as ventilation rates and both ambient and barn temperatures increase (ambient and barn

temperatures were positively and strongly correlated, $r^2 = 0.88$, $p\text{-value} < 0.0001$). The barn exhaust temperatures for all seasons were plotted against the corresponding ventilation rates (Figure 2.6). Generally, greater temperature ranges tended to occur at ventilation rates between 500 and 1000 $\text{m}^3 \text{min}^{-1}$ but overall there was a fairly strong positive correlation ($r^2 = 0.65$, $p\text{-value} < 0.0001$), meaning that 65% of the variation in ventilation rates can be explained by the exhaust temperature. It is noted that the temperature at the fan exhaust may differ from the location in the barn where the fan stage control operates. Although not plotted, ambient temperature had an even higher correlation with total ventilation rate ($r^2 = 0.70$, $p\text{-value} < 0.0001$). Relative humidity was negatively correlated with ventilation rate as well but with a much smaller r^2 value of 0.32 ($p\text{-value} < 0.0001$), meaning that little of the variation is explained by this parameter.

The $\text{NH}_3\text{-N}$ and H_2S normalized emission rates showed low correlation to one another ($r^2 = 0.20$, $p\text{-value} < 0.0001$). The normalized H_2S emission rate was well correlated with the measured gas concentration ($r^2 = 0.55$, $p\text{-value} < 0.0001$) and showed almost no dependence on the total ventilation rate ($r^2 = \sim 0$, $p\text{-value} = 0.72$). On the other hand, normalized $\text{NH}_3\text{-N}$ emissions showed a higher correlation with the total ventilation rate ($r^2 = 0.33$, $p\text{-value} < 0.0001$) than the measured gas concentration ($r^2 = 0.17$, $p\text{-value} < 0.0001$). These correlations, along with the diurnal profiles shown in Figure 2.5, indicate that the H_2S concentration inside the barn does not tend to buildup when fewer fans are running while the $\text{NH}_3\text{-N}$ concentration may accumulate. Relative humidity and barn temperatures were not correlated at all with either normalized H_2S emission rate ($r^2 = 0.01$ and $r^2 = \sim 0$, respectively).

Time series graphs (Figure 2.7) were created in order to further examine the relationship between ventilation rates and barn temperature as well as gaseous concentration levels. The spring experimental period was chosen due to the large variation in flow rates during the measurement period. The ventilation rates (sum of all flow rates for the fans in operation) during this period ranged from 251 – 1996 m³ min⁻¹. The ventilation rates change in accordance with the temperature, lagging slightly.

As indicated by Pearson's Correlation Coefficients, the measured NH₃-N and H₂S gas concentrations are both inversely related to the ventilation rates. Data gaps in the measured H₂S and NH₃-N occurred when the analysis instruments were being spanned and/or background samples were being measured. Toward the end of the graph, for approximately a 24-hour period (April 12-13), the ventilation rate remains constant. During this period, the H₂S concentration levels fluctuate slightly but remain relatively steady; however, the NH₃-N concentration decreases from ~10 ppm to ~6 ppm around 02:30 and remains near this level throughout the remainder of this 24-hour period. Examining the data, no significant changes were recorded for static pressure, ambient temperature, barn temperature, or relative humidity. The instrument span checks indicated no errors in the analyzer. The reason for the change in concentration is unknown.

Total fan ventilation rates were also plotted against NH₃-N and H₂S emission rates in Figure 2.8 and Figure 2.9, respectively to determine possible variations from the ventilation rates. During the winter and fall, when ventilation rates were on average lower than spring and summer (Table 2.2), emission rates for both NH₃-N and H₂S increase linearly until both 91 cm fans are running steadily (≤ 500 m³ min⁻¹) and then

stabilize at higher ventilations. During the spring, $\text{NH}_3\text{-N}$ emissions increase linearly (with some variation) as ventilation increases up to $\sim 1000 \text{ m}^3 \text{ min}^{-1}$ (3 fans running) and then stabilizes. The H_2S emission rates during spring do not exhibit this pattern; there is little difference between emission rates at various ventilation rates. During the summer, when ventilation rates were highest and usually two or more fans were running, $\text{NH}_3\text{-N}$ emission rates remained steady while H_2S increased slightly. As shown in Figures 2.8 and 2.9, the correlation between total fan ventilation rates and normalized emission rates for each gas varies by season. When seasonal variation is not considered (Table 2.6), there is almost no correlation between the ventilation rates and H_2S normalized emission rates ($r^2 = \sim 0$, p-value = 0.72). The correlation is higher for $\text{NH}_3\text{-N}$ normalized emission rates during for all four seasons ($r^2 = 0.33$, p-value < .0001).

2.5 Conclusions

Data was collected continuously for a one-week period during each season (i.e., fall, winter, spring, summer) for one year from a finishing swine confinement house at a commercial hog farm in eastern North Carolina. The primary objective of this research initiative was to investigate and evaluate the variability of ammonia and hydrogen sulfide emissions with respect to diurnal and seasonal variations as well as the influence of meteorological factors.

Average $\text{NH}_3\text{-N}$ concentrations were highest during the winter and spring sampling periods, 8.9 and 8.4 ppm, respectively. The higher concentration values during the winter may be attributed to less airflow through the building compared to other seasons, causing a buildup of the gas to occur. It is likely that the large concentrations measured in the spring are due to the age and weights of the animals housed in the barn.

The lowest concentrations measured at the fan exhaust occurred during the summer experimental, when ventilation rates were higher. Measured H₂S concentrations were highest during the winter and lowest during the summer, 673 and 47 ppb, respectively. The average H₂S concentration was 6-14 times less during the summer sampling period as opposed to the other seasons. Generally, the H₂S concentrations were approximately an order of magnitude less than NH₃-N during winter, spring, and fall, and two orders of magnitude smaller during the summer season.

Calculated normalized emission rates for both NH₃-N and H₂S were highest during the winter, 33.6 and 4.2 g day⁻¹, respectively. Normalized emissions were lowest during the fall season for NH₃-N (24.3 g day⁻¹ AU⁻¹) and the summer season for H₂S (1.2 g day⁻¹ AU⁻¹). The normalized emission rate for H₂S from the barn was ~3.5 times higher during the winter season than summer and the normalized emission rate for NH₃-N was almost three times higher in winter than fall, indicating that emissions may not increase linearly with animal mass.

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Table 2.1. Sampling periods for NH₃-N and H₂S barn emission measurements and information for hogs housed inside the barns.

<i>Season</i>	<i>Sample Dates</i>	<i>Number of Hogs</i>	<i>Number of Weeks in Rotation</i>	<i>Average Weight^{a,b}</i>	<i>Total Weight^a</i>
Winter	Feb 22-27, 2005	851	8	57.6	48963
Spring	Apr 07-14, 2005	842	14	87.8	73895
Summer	Jun 19-24, 2005	896	4	37.9	33952
Fall	Oct 26 –31, 2005	889	5	43.2	38390

^a Measured in units of kg

^b Weighted average for hogs of different weights brought into the barn on different dates.

Table 2.2. Simple statistics for barn measurements made for experimental periods during four different seasons.

	H ₂ S Concentratio n ^a (ppb)	NH ₃ -N Concentratio n ^a (ppm)	Ventilation Rate ^{b, c} (m ³ min ⁻¹)	Fan Outlet Temperat ure ^a (°C)	Ambient Temperat ure (°C)	Ambient Relative Humidity %
Winter 2005						
Average (Std Dev.)	673 (282)	8.91 (4.61)	328 (170)	19.7 (2.5)	5.5 (4.8)	83 (17)
Range	0 - 982	0.65 – 14.55	87 – 778	13.1 – 24.0	-3.4 – 16.2	38 - 100
Spring 2005						
Average (Std Dev.)	429 (223)	8.43 (2.40)	726 (380)	22.3 (2.8)	13.7 (5.8)	75 (24)
Range	55 - 996	3.14 – 14.14	251 – 1996	14.6 – 27.9	3.7 – 26.9	22 – 98
Summer 2005						
Average (Std Dev.)	47 (18)	2.45 (1.14)	1024 (684)	26.0 (2.6)	22.3 (4.9)	73 (19)
Range	2 – 113	0.58 – 6.59	248 - 2273	12.4 – 31.4	12.1 – 32.3	36 - 97
Fall 2005						
Average (Std Dev.)	304 (88)	4.27 (0.71)	253 (119)	19.0 (2.8)	9.1 (5.1)	76 (23)
Range	6 -527	3.27 – 7.63	101 – 491	14.0 – 25.8	1.0 – 21.5	20 -96

^a Measured at 91 cm fan outlet^b Flow from two 91 cm fans and three 122 cm fans summed together.^c Multiply by 35.31 to obtain cfm (ft³ min⁻¹)

Table 2.3. Statistical summary table of total and normalized average daily NH₃-N and H₂S barn emission rates for each season

Season	Total Emission Rate ^a			Normalized Emission Rate ^{a,b}		
	Mean ^c	Minimum	Maximum	Mean ^c	Minimum	Maximum
NH ₃ -N						
Winter 2005	3290 (2143)	54	8930	33.6 (21.9)	0.5	91.2
Spring 2005	4519 (1639)	1550	14514	30.6 (11.1)	10.5	98.2
Summer 2005	1653 (840)	626	8935	24.3 (12.4)	9.2	131.6
Fall 2005	904 (568)	299	3027	11.8 (7.4)	3.9	39.4
H ₂ S						
Winter 2005	412 (208)	0	887	4.2 (2.1)	0	9.1
Spring 2005	481 (142)	113	859	3.3 (1.0)	0.8	5.8
Summer 2005	82 (49)	2	287	1.2 (0.7)	0	4.2
Fall 2005	133 (42)	0	252	1.7 (0.5)	0	3.3

NH₃-N flux = (14/17) NH₃ flux

^a Units of flux are g day⁻¹

^b AU (Animal Units) = 500 kg Live Animal Weight

^c Numbers in parenthesis represent one standard deviation

Table 2.4. Normalized NH₃-N confinement house emission rates from previous studies compared with this study.

<i>Study</i>	<i>Season</i>	<i>Facility Type</i>	<i>Manure Pit Type</i>	<i>Ventilation Type</i>	<i>Normalized NH₃-N^a Emission Rate^b</i>
Heber et al. (1997)	Jan. – Mar.	Finish	Deep Pit	Natural	34
Heber et al. (2000)	Mar. – May	Finish	Deep Pit	Mechanical	54
Heber et al. (2000)	Mar. – May	Finish	Deep Pit	Mechanical	54
Heber et al. (2000)	Jun. – Sept.	Finish	Deep Pit	Mechanical	120
Heber et al. (2000)	Jun. – Sept.	Finish	Deep Pit	Mechanical	78
Schmidt et al. (2002)	Feb. – Mar.	Finish	Deep Pit	Mechanical	6.6
Schmidt et al. (2002)	Jun. – Jul.	Finish	Deep Pit	Natural	66.0
Lim et al. (2004)	May - July	Finish	Pit Recharge, 1 week	Mechanical	8.2
Lim et al. (2004)	May - July	Finish	Pit Recharge, 2 week	Mechanical	9.9
Lim et al. (2004)	Mar. - May	Finish	Pit Recharge, 6 week	Mechanical	9.1
Jacobson et al. (2006)	-	Finish	Deep Pit	Mechanical	20.4
Jacobson et al. (2006)	-	Finish	Pull-Plug	Mechanical	9.3
This Study	Feb.	Finish	Pit Recharge, 1 week	Mechanical	33.6
This Study	Apr.	Finish	Pit Recharge, weekly	Mechanical	30.6
This Study	Jun.	Finish	Pit Recharge, weekly	Mechanical	24.3
This Study	Oct.	Finish	Pit Recharge, weekly	Mechanical	11.8

^a Multiply by 1.214 to obtain NH₃ emission rate^b Measured in g day⁻¹ 500 kg live animal weight (LAW)⁻¹

Table 2.5. Concentrations and emissions of hydrogen sulfide from barn exhaust systems from previous studies compared with this study.

<i>Study</i>	<i>Season</i>	<i>Manure Pit Type^a</i>	<i>Total Live Animal Weight^b</i>	<i>Ventilation Type</i>	<i>Ventilation Rate^c</i>	<i>Number of Samples</i>	<i>Average Daily Mean Concentration^d</i>	<i>Normalized H₂S Emission Rate^e</i>
Zhu et al. (2000)	September.	Full	44 990	Mechanical	218	7	414	2.00 ^f
Zhu et al. (2000)	Sept.	Full	43 640	Natural	501	7	271	3.11 ^f
Heber et al. (1997)	Jan. – Mar.	Full	-	Natural	-	1500	180	0.84
Ni et al. (2002)	June – Sept.	Full	48 783	Mechanical	2637	529	173	7.0 ^f
Schmidt et al. (2002)	Winter	Full	102 058	Mechanical	-	-	6	0.007 ^f
Jacobson et al. (2006)		Full	-	Mechanical	-	-	434	3.4
Jacobson et al. (2006)		Pull-plug	-	Mechanical	-	-	588	4.3
This Study	Feb.	Shallow	48 963	Mechanical	328	385	632	4.2
This Study	Apr.	Shallow	73 895	Mechanical	726	617	441	3.3
This Study	Jun.	Shallow	33 952	Mechanical	1024	415	47	1.2
This Study	Oct.	Shallow	38 390	Mechanical	253	432	304	1.7

^aFull = deep pit; Shallow = Pit recharge (1 per week)

^bMeasured in kg

^cMeasured in m³ min⁻¹ [Multiply by 35.31 to obtain cfm (ft³ min⁻¹)]

^dMeasured in ppb

^eMeasured in g day⁻¹ per 500 kg animal units (AU)⁻¹

^fCalculated based on data available in literature.

Table 2.6. Pearson's Correlation Coefficients calculated to show relationships between gas concentrations, normalized gas emission rates, fan flow rate, and meteorological parameters.

	H ₂ S Conc.	H ₂ S Normalized Emissions	NH ₃ -N Conc.	NH ₃ -N Normalized Emissions	Total Ventilation Rate	Air Temp.	<i>Barn Temp.</i>
H ₂ S Normalized Emission	0.74 ^a 0.55 ^b <.0001 ^c 1817 ^d						
NH ₃ -N Concentration	0.67 0.45 <.0001 1575	0.68 0.46 <.0001 1577					
NH ₃ -N Normalized Emission	-0.15 0.02 <.0001 1687	0.45 0.20 <.0001 1577	0.41 0.17 <.0001 1577				
Total Ventilation Rate	-0.46 0.21 <.0001 1818	-0.01 ~0 0.72 1819	-0.29 0.08 <.0001 1577	0.58 0.33 <.0001 1577			
Air Temperature	-0.66 0.44 <.0001 1818	-0.18 0.03 <.0001 1819	-0.34 0.12 <.0001 1577	0.56 0.31 <.0001 1577	0.84 0.70 <.0001 1995		
Barn Temperature	-0.41 0.17 <.0001 1657	0.09 0.01 0.0003 1658	-0.09 0.01 0.0013 1416	0.64 0.41 <.0001 1416	0.81 0.65 <.0001 1827	0.94 0.88 <.0001 1827	
Relative Humidity	0.33 0.11 <.0001 1818	-0.03 ~0 0.2797 1819	0.07 0.0035 0.0121 1577	-0.54 0.29 <.0001 1577	-0.56 0.32 <.0001 1995	-0.59 0.35 <.0001 1995	-0.56 0.32 <.0001 1827

^a Correlation coefficient (r): measure of the strength of the relationship between two variables.

^b Coefficient of Determination (r²): percent of variation that can be explained by the predictor variable

^c p-value: measure of probability that result occurred strictly by chance.

^d Number of observations for comparison (n)

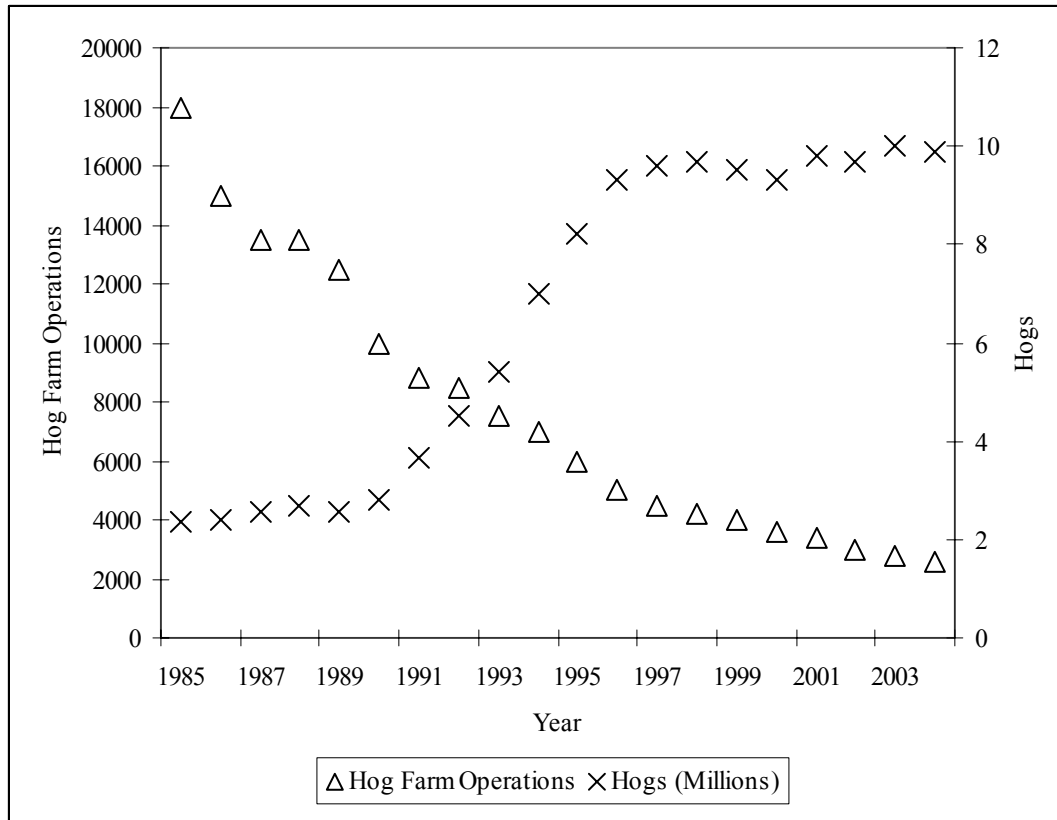


Figure 2.1. Number of North Carolina hog farming operations and hogs from 1985 to 2004.

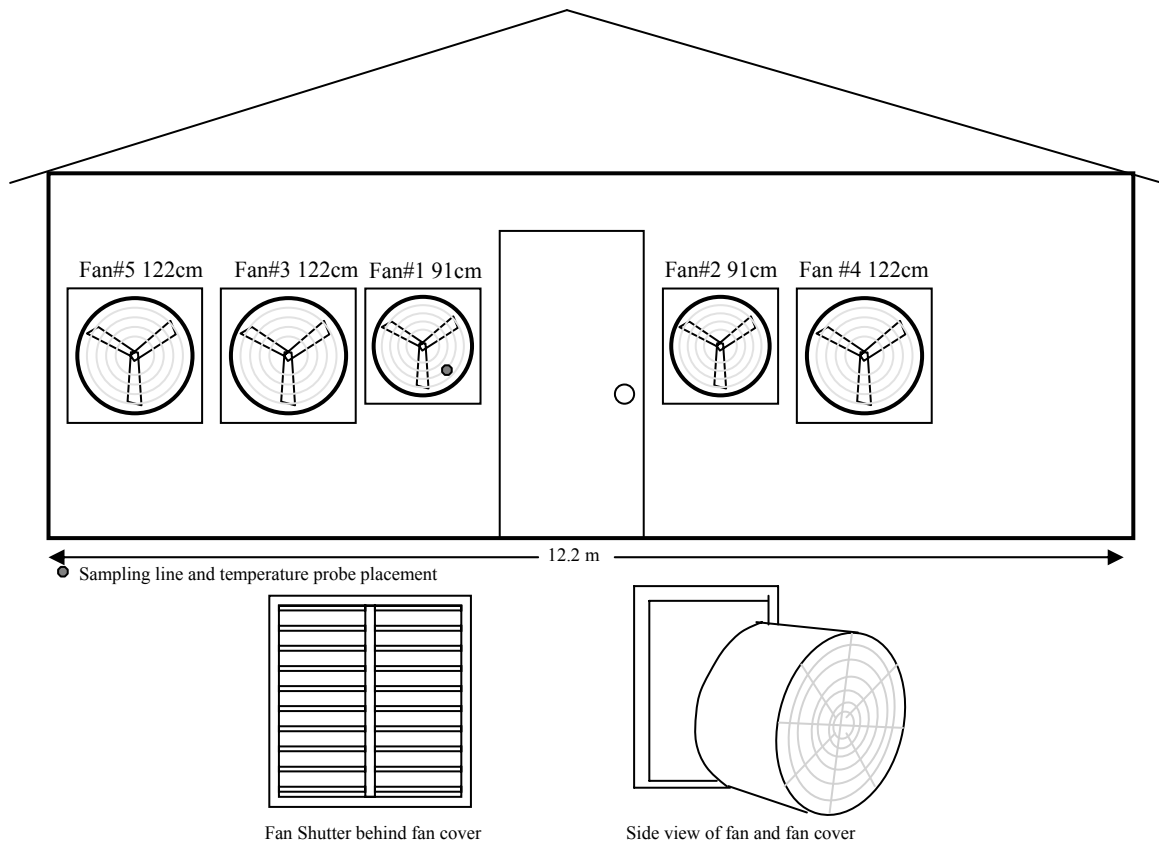


Figure 2.2. Schematic of mechanically ventilated fan exhaust system at experimental site. Fans are numbered in the order in which they are staged to turn on.

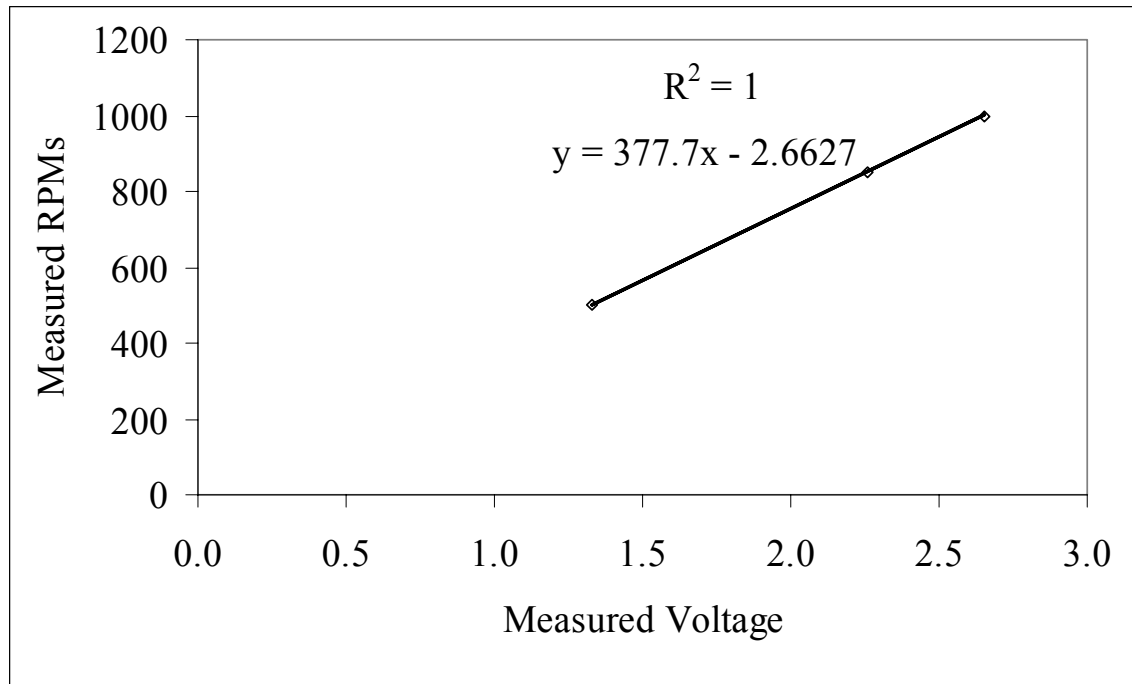
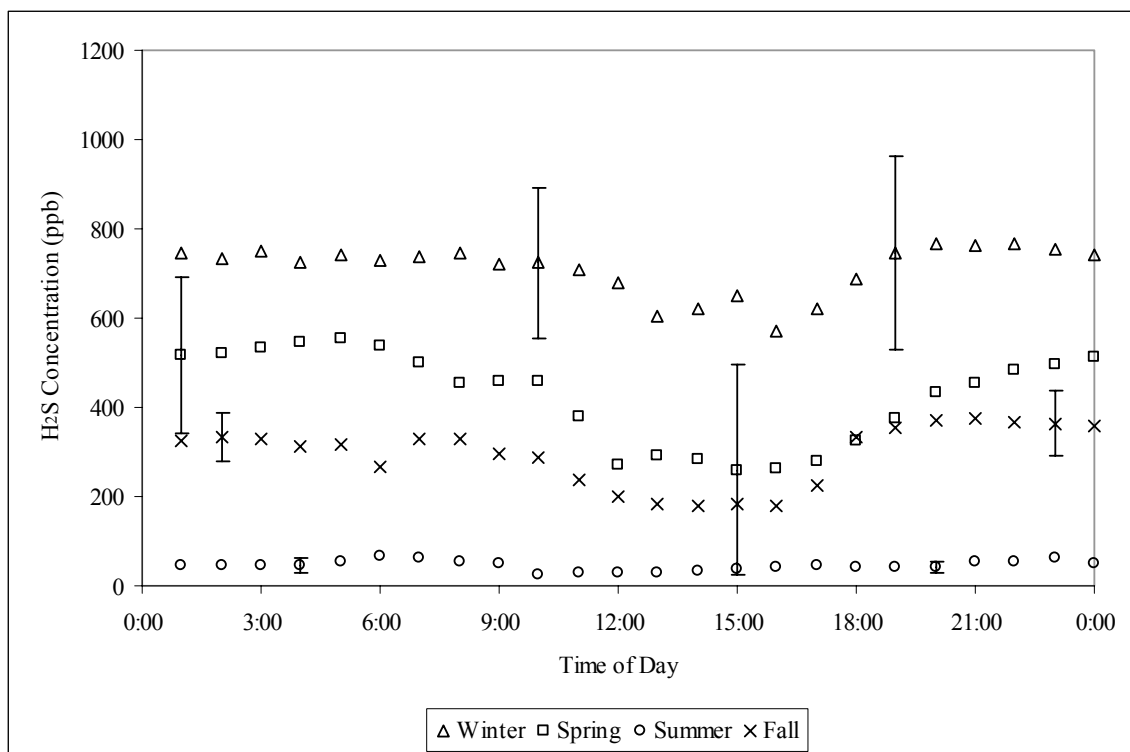
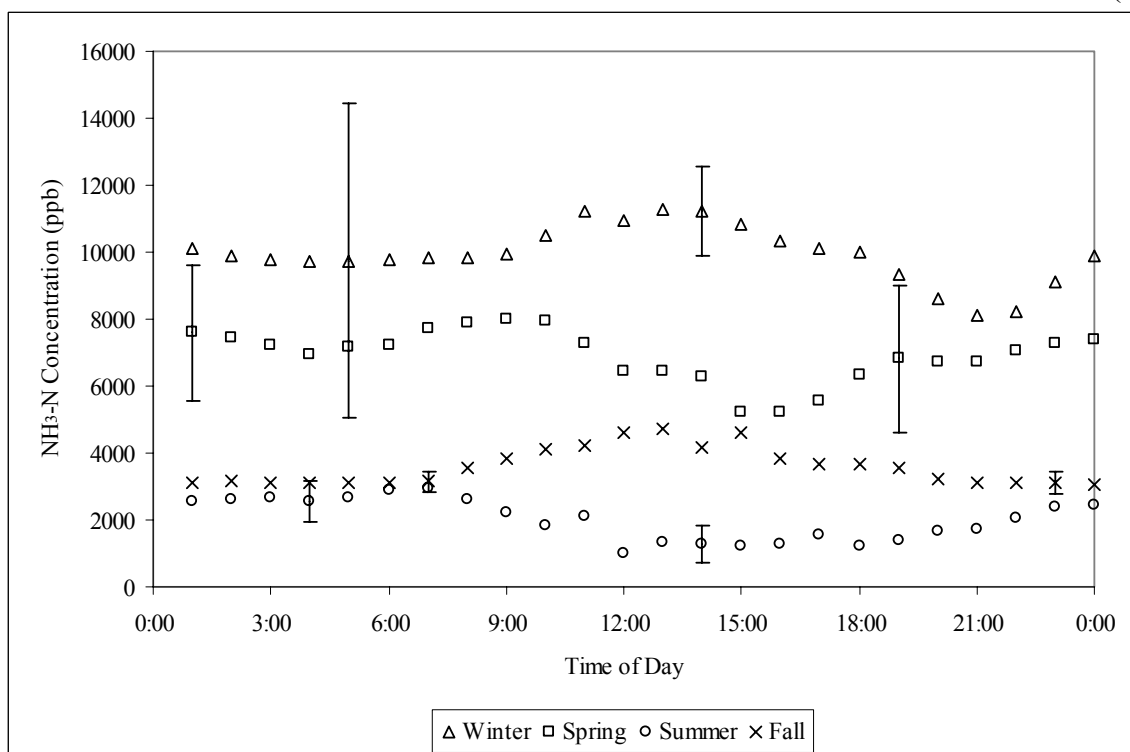


Figure 2.3. Measured voltage of a VDC Motor used to monitor fan “on/off” times and speed plotted against measured RPMs at that voltage. The conversion is made using the given equation for the respective motor.

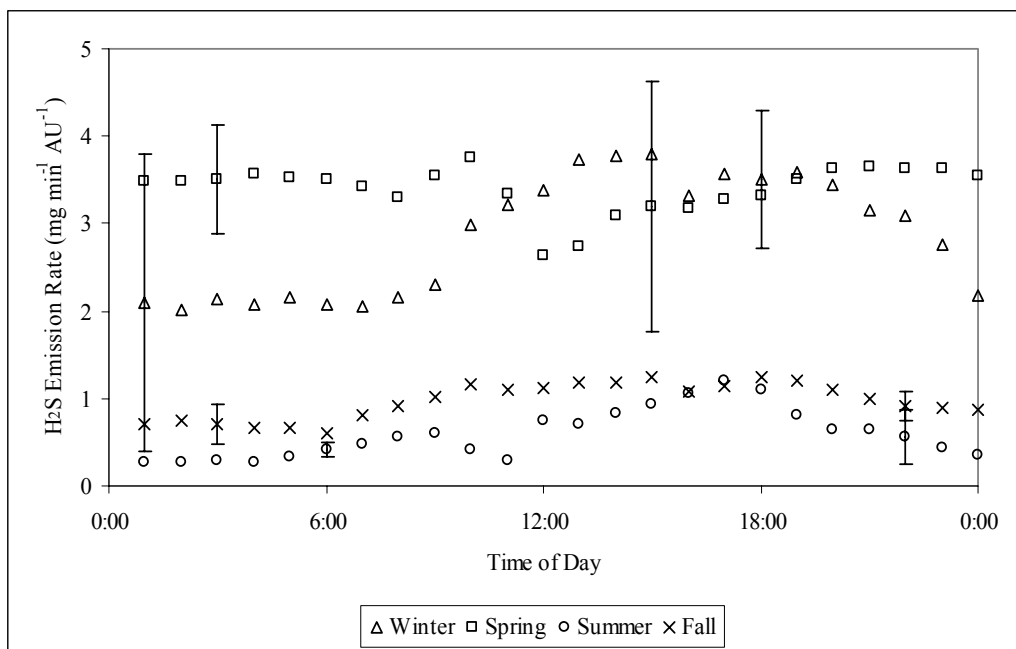


(a)

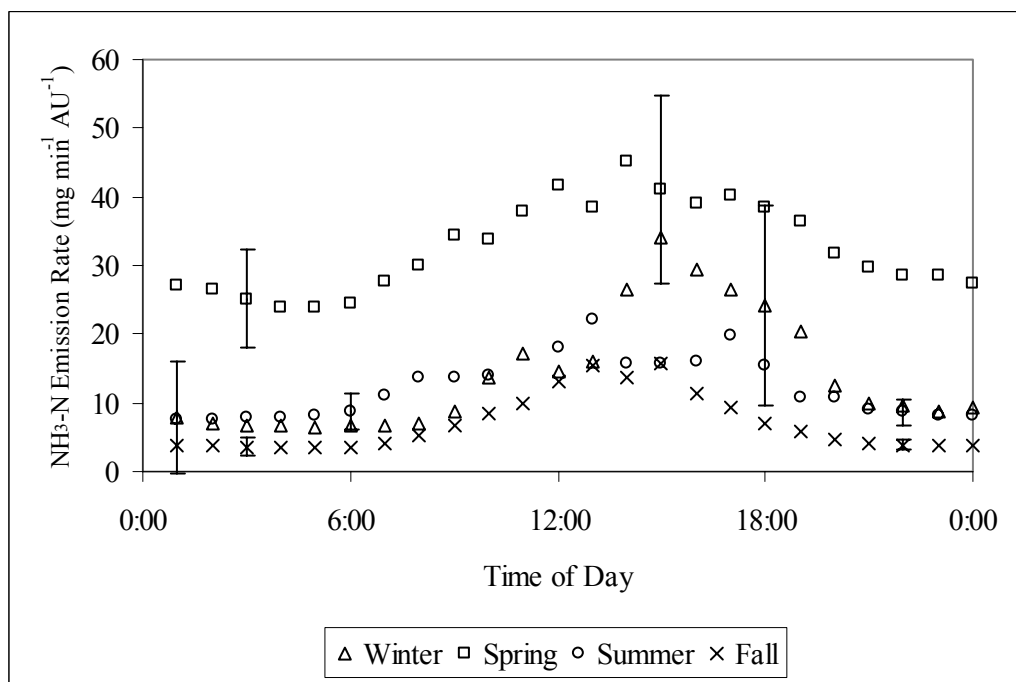


(b)

Figure 2.4. Seasonally averaged diurnal variations for (a) H_2S and (b) NH_3-N concentrations measured at fan ventilation exhaust. Randomly selected data points show variability in measurements. Each error bar represents one standard deviation.



(a)



(b)

Figure 2.5. Seasonally averaged diurnal variations for (a) H₂S and (b) NH₃-N normalized emission rates from hog barn. Randomly selected data points show variability in measurements. Each error bar represents one standard deviation.

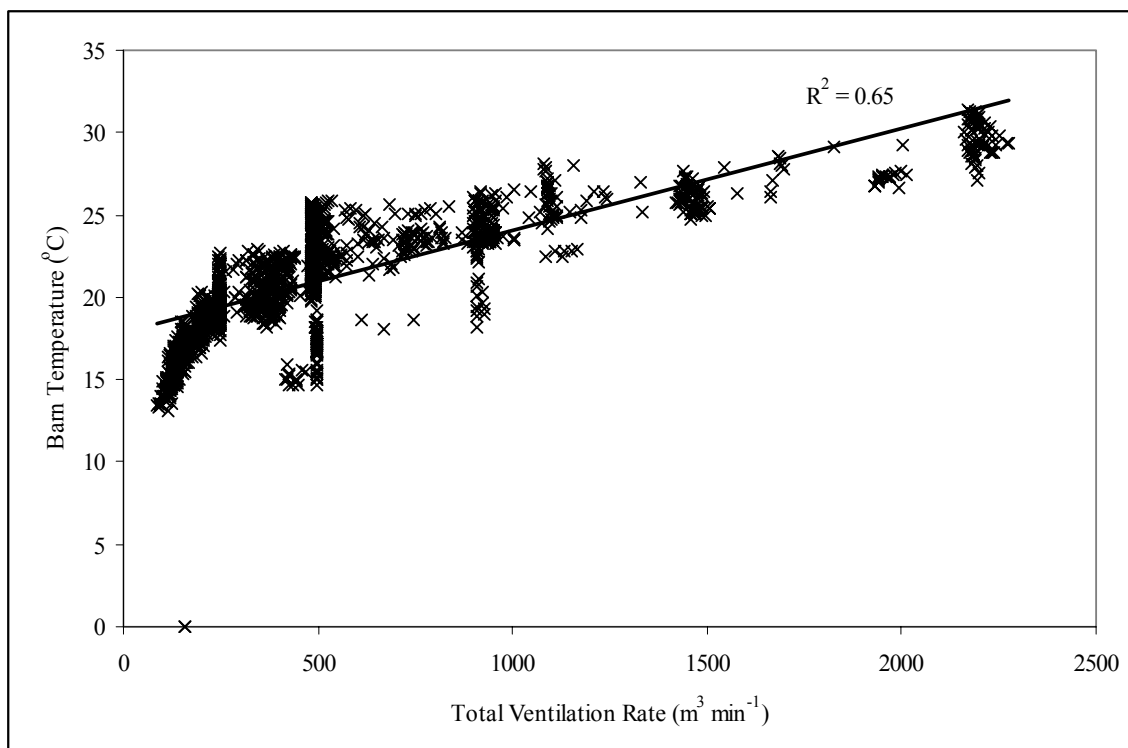
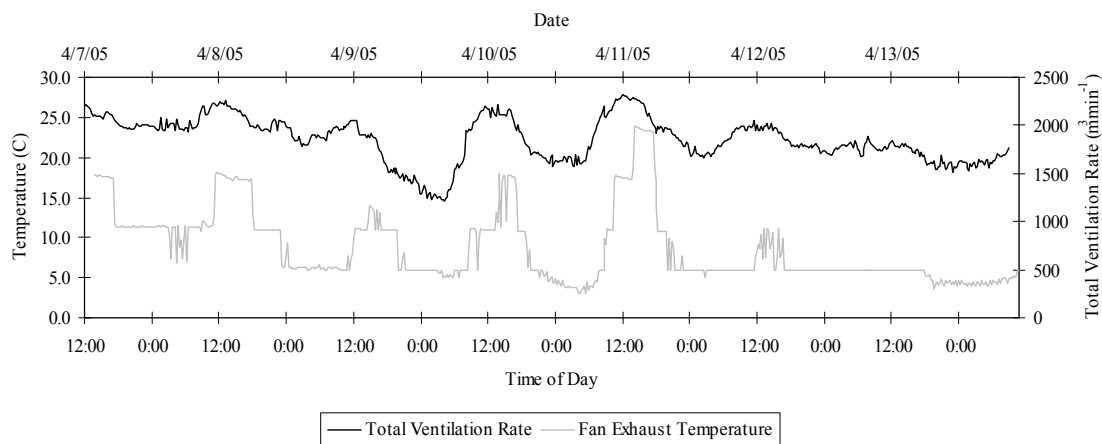
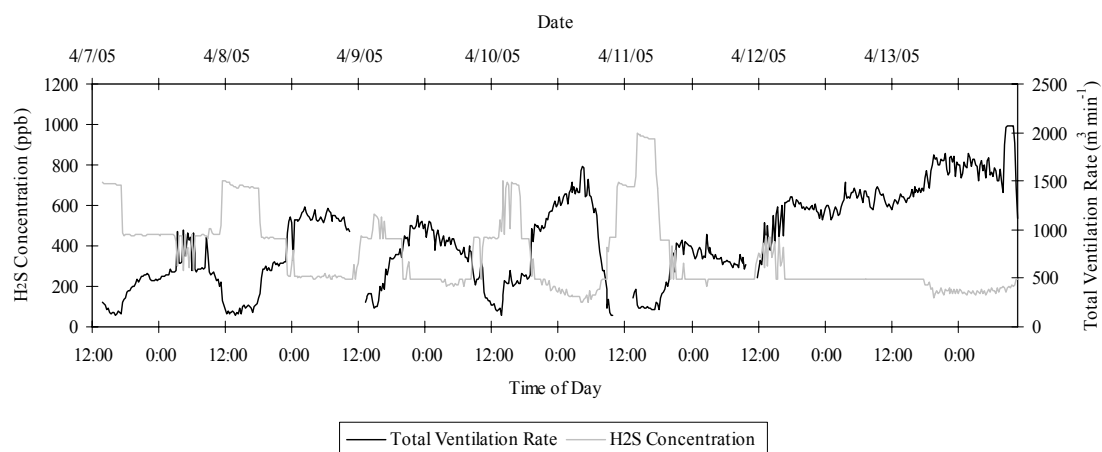


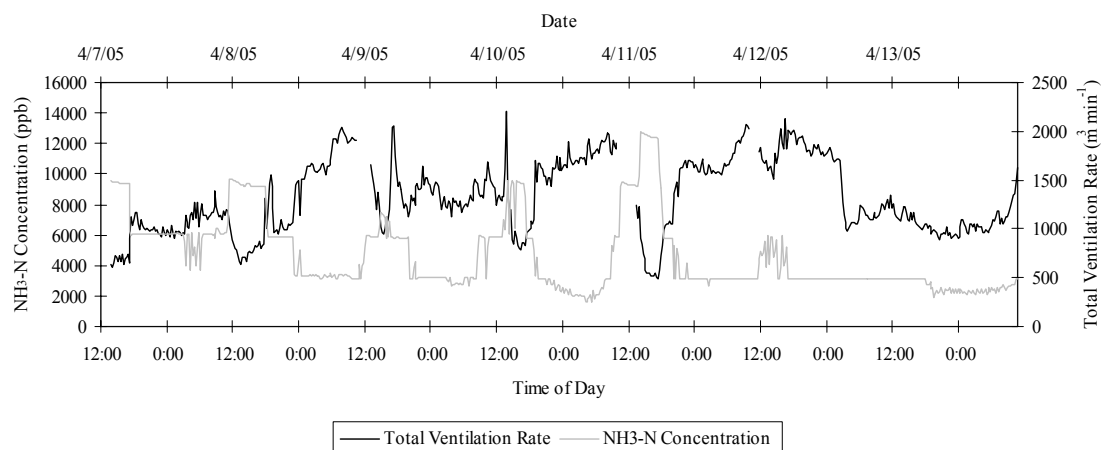
Figure 2.6. Measured barn exhaust temperature plotted against total fan exhaust ventilation rate. Data from all seasons is included.



(a)



(b)



(c)

Figure 2.7. Time series relationship between fan flow rate and barn temperature and gas concentrations measured at the barn exhaust fan.

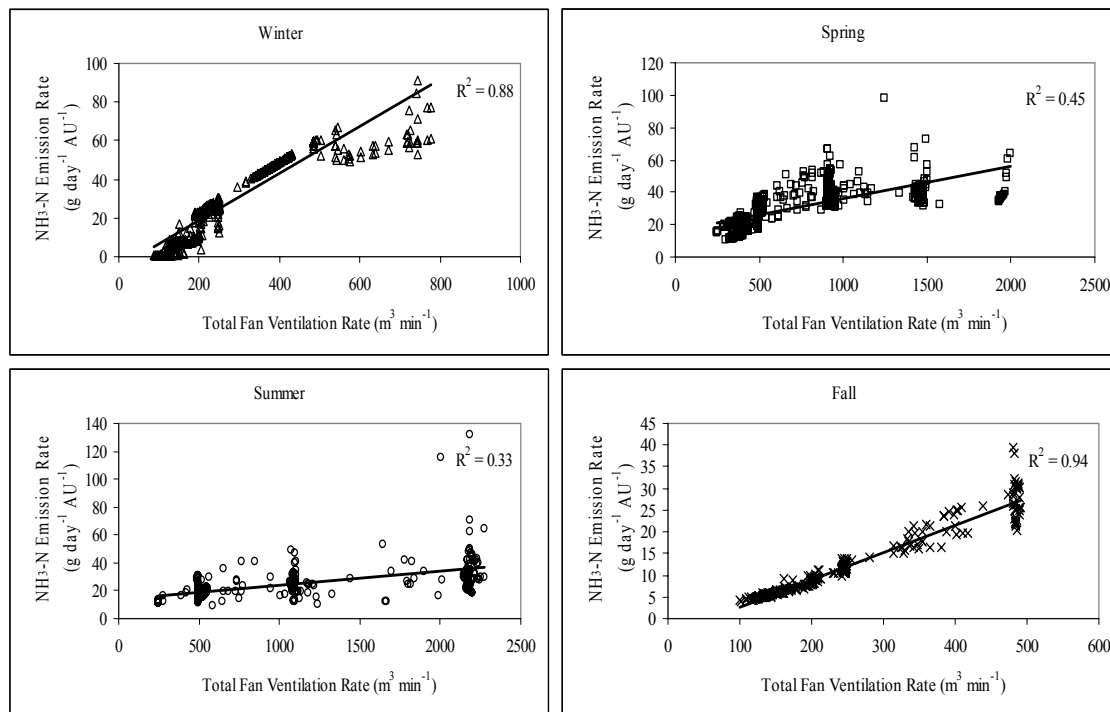


Figure 2.8. Emission rates of NH₃-N plotted against total fan ventilation rates for each season.

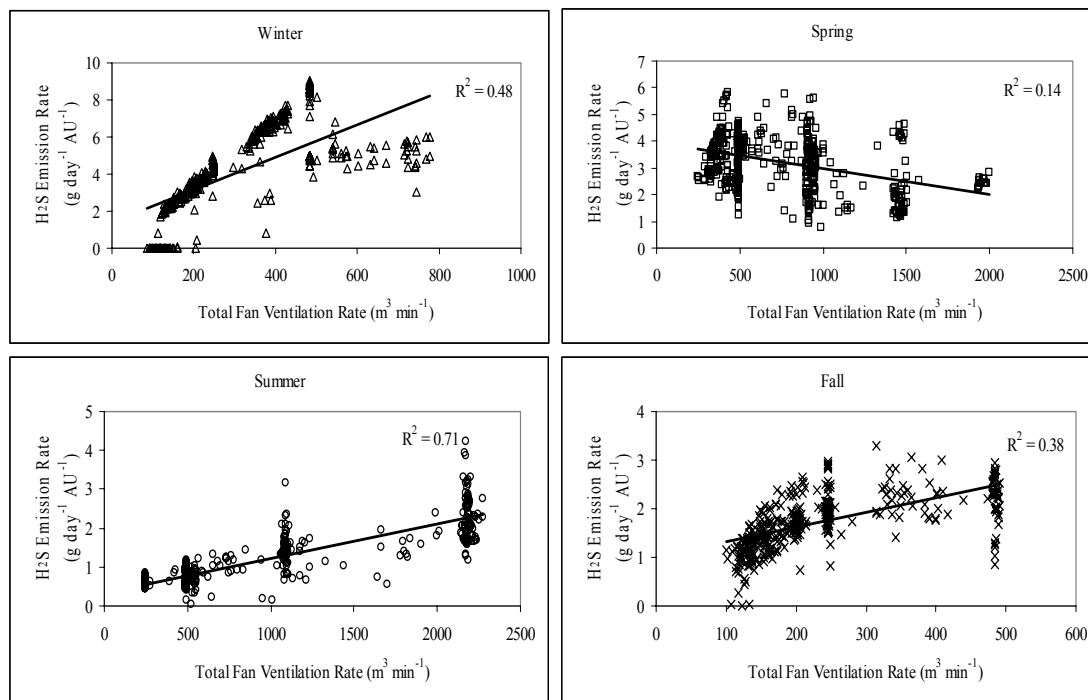


Figure 2.9. Emission rates of hydrogen sulfide plotted against total fan ventilation rates for each season

**CHAPTER III. CHARACTERIZING AMMONIA AND HYDROGEN
SULFIDE EMISSIONS FROM A SWINE WASTE
TREATMENT LAGOON IN NORTH CAROLINA**

by

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Abstract

Emissions of atmospheric ammonia-nitrogen ($\text{NH}_3\text{-N}$, where $\text{NH}_3\text{-N} = (14/17)\text{NH}_3$) and hydrogen sulfide (H_2S) from a commercial anaerobic swine waste treatment lagoon ($30,630 \text{ m}^2$) were measured over a one year period. Continuous simultaneous measurements were made at the lagoon using a dynamic flow-through chamber system for ~ 1 week during four seasons, Oct-Nov 2004 (fall), February 2005 (winter), April 2005 (spring), and June 2005 (summer) in an effort to examine diurnal and seasonal variability and the respective relationships of $\text{NH}_3\text{-N}$ and H_2S emissions to lagoon physiochemical properties. Continuously measured lagoon physiochemical parameters include lagoon surface temperature and lagoon pH. Aqueous lagoon samples were collected daily and analyzed for Total Kjeldahl Nitrogen (TKN), Total Ammoniacal Nitrogen (TAN), and total sulfide concentration (mg L^{-1}). TKN, TAN, and sulfide concentrations ranged from 400-650, 360-590, and 0.1-13.0 mg L^{-1} , respectively. For $\text{NH}_3\text{-N}$, the largest fluxes were observed during the summer ($> 4200 \mu\text{g N m}^{-2} \text{ min}^{-1}$). During the fall and spring, average $\text{NH}_3\text{-N}$ fluxes were 1634 ± 505 and $> 2495 \mu\text{g N m}^{-2} \text{ min}^{-1}$, respectively. The lowest fluxes were observed during the winter where average flux values were $1290 \pm 246 \mu\text{g N m}^{-2} \text{ min}^{-1}$. The lowest fluxes for H_2S were also observed during the winter season, $\sim 0.0 \mu\text{g m}^{-2} \text{ min}^{-1}$. Average fluxes increased during the fall ($0.3 \pm 0.1 \mu\text{g m}^{-2} \text{ min}^{-1}$) and spring ($0.5 \pm 1.0 \mu\text{g m}^{-2} \text{ min}^{-1}$), and highest flux values were observed during the summer ($5.3 \pm 3.2 \mu\text{g m}^{-2} \text{ min}^{-1}$). Generally, the lagoon emissions for H_2S were ~ 3 -4 orders of magnitude less than $\text{NH}_3\text{-N}$. The gas fluxes were related to various physico-chemical parameters including the pH and near-surface temperature of the lagoon, and the aqueous concentration of the respective gas.

3.1 Introduction

Emissions of potentially harmful gases such as ammonia (NH_3) and hydrogen sulfide (H_2S) from confined animal feeding operations (CAFOs) have become a major problem in recent years in North Carolina as changes in crop and livestock production methods are in turn changing emissions of trace gases (e.g., sulfur and nitrogen species) into the atmosphere (Aneja et al., 2006a). Notably, the swine industry has grown significantly since the early 1990s, with an increase in inventory from 2.5 million to ~9.4 million animals, and is now a major animal agricultural industry in the state. However, as the number of hogs increased, the number of hog operations decreased, from 18 000 in 1985 to 2600 by 2004. The shift in the hog farming industry over the past two decades is illustrated in Figure 3.1, with the vast majority of the hog farms in North Carolina clustered in the southeastern piedmont region of the state (Figure 3.2). Currently, there are more than 1400 operations with more than 1000 head, accounting for almost 99% of the state inventory (<http://www.nass.usda.gov/QuickStats/>). Public concerns about potential environmental and health effects of air emissions from CAFOs have increased in parallel with the growth and consolidation of this industry (Aneja et al., 2006a).

Ammonia is a by-product of microbial decomposition of the organic compounds in manure and nitrogen occurs as both unabsorbed nutrients in manure and as urea in urine (U.S. EPA, 2001). Ammonia released from near-surface sources (i.e. waste treatment lagoons) into the atmosphere generally has a relatively short lifetime of ~1-5 days (Warneck, 2000) and may deposit near the source through dry or wet deposition. However, ammonia can also participate in atmospheric reactions (e.g. gas-to-particle conversion) once airborne, forming ammonium aerosols such as ammonium sulfate, -

nitrate, -chloride, which tend to have longer atmospheric residence lifetimes (~1-15 days) owing to a decrease in dry deposition velocity (Aneja et al., 1998) and therefore may be transported and deposited further downwind from the source. An environmental concern in eastern North Carolina that has been associated with ammonium aerosols is deposition into sensitive coastal river and coastal ecosystems where nitrogen loading may lead to enhanced eutrophication and soil acidification, which may in turn upset plant nutrient balances near sources (Paerl, 1997).

Hydrogen sulfide, another major compound of concern, is a colorless, potentially lethal gas released from swine manure (U.S.EPA, 2004). It is produced as manure decomposes anaerobically, resulting from the mineralization of organic sulfur compounds as well as the reduction of oxidized inorganic sulfur compounds such as sulfate by sulfur-reducing bacteria (U.S. EPA, 2001). The U.S. Center for Disease Control (CDC) warns that brief exposures to high concentrations (> 500 parts per million, ppm) can cause unconsciousness or death (ATSDR, 2004). Campagna et al. (2004) have reported a correlation between elevated ambient H₂S concentrations and hospital visits for respiratory diseases. Donham et al. (1982) reported that hydrogen sulfide appeared to be the main toxic substance in liquid manure associated with death and illness for people with acute exposure to gases emanating from liquid manure. With a low odor threshold ranging from 0.0005 to 0.3 ppm (ATSDR, 2004), it is also one of the gases released from swine facilities that is associated with odor complaints due to its characteristic “rotten egg” smell. Potential negative health effects have been identified in production workers and neighboring residents that include respiratory illnesses such as bronchitis and asthma, and increased psychological stress (Schiffman, 1998).

Significant efforts have been devoted to understanding emissions of ammonia from these operations (Harper et al., 2000; Aneja et al., 2000, 2001a,b, 2006). Arogo et al. (2003) have reviewed measurement techniques and studies undertaken to estimate NH_3 emissions from both swine lagoons and animal confinement houses. Emissions of hydrogen sulfide from animal confinement houses have been estimated (Zhu et al., 2000; Ni et al., 2002); however, few studies have reported emissions from waste storage treatment lagoons (Zahn et al., 2001; Lim et al., 2003; Byler et al., 2004), none from farms in the southeastern U.S. Various factors, such as differing animal and crop production, farming activities and regional climates, may affect the emissions of gases into the atmosphere. Emissions estimates generated for one set of conditions or for one type of CAFO may not translate readily to others. It is therefore important for comprehensive emissions measurements to be made from different types of operations.

The primary objective of this research initiative was to investigate and evaluate the variability of ammonia and hydrogen sulfide emissions with respect to diurnal and seasonal variations as well as the influence of meteorological and physico-chemical factors. Data presented here was collected continuously using in situ measurement techniques for a one-week period during each season (i.e., fall, winter, spring, summer) for one year from an anaerobic swine lagoon at a finishing hog farm in eastern North Carolina.

3.2 Methods and Materials

3.2.1 Physiographic Location and Farm Description

The experimental site is an operational commercial swine finishing farm located in Jones County, NC in the southeastern coastal plain region of the state, where the majority of hog farming operations are located. The on-site waste storage treatment lagoon is 30,630 m² and the farm maintains eight fan-ventilated confinement houses. Generally, the hogs are rotated out of each house approximately every 18 weeks, weighing ~22-24 kg upon arrival and gaining ~5 kg per week. There are ~800 to ~900 animals housed in each barn and rotations are staggered for each house. The farm utilizes a conventional “lagoon and spray” technology as its primary means of handling effluent, which is the most widely used method in North Carolina. Effluent is flushed directly from the hog barns once per week into the storage lagoon and a portion of the stored lagoon wastewater is recycled to recharge the pit. Lagoon wastewater is also periodically used as spray over on-site agricultural crops for nutrient enrichment purposes.

3.2.2 Dynamic Flow-Through Chamber System and Gas Analyzers

A flow-through dynamic chamber system with a variable-speed motor-driven continuous impeller stirrer (Aneja et al., 2000) was employed to determine ammoniacal nitrogen (NH₃-N) and hydrogen sulfide (H₂S) flux from the lagoon. The translucent plastic cylindrical chamber, 0.25 m internal diameter, 0.46 m internal height of chamber above water or soil, and volume 0.025m³, is fitted into a circular hole cut into the center of a 0.61 x 0.61 m floating ½” thick ultra-high molecular weight (UHMW) polyethylene platform. The chamber penetrated into the lagoon ~7 cm, creating an internally closed system. The platform is supported by 0.15 m diameter by 1.68 m length PBC piping for

floatation, designed to sit a few centimeters above the lagoon in order to minimize experimental effects and simulate atmospheric conditions at the lagoon surface as accurately as possible. A schematic of the chamber system is shown in Figure 3.3.

The chamber was lined internally with a 2 mil fluorinated ethylene propylene (FEP) Teflon sheet to reduce chemical reactions and build up of temperature inside the chamber. Compressed zero-grade air was used as a carrier gas and pumped through the chamber at a variable flow rate of ~ 9 -12 L min⁻¹ utilizing a Model 810-S Mass Trak Flow Controller (Sierra Instruments, Monterey, CA). The in-flowing air was carried through a 1/4" o.d., 5/32" i.d Teflon FEP sample line to the chamber. The air inside the chamber is ideally well-mixed by a variable-speed motor-driven Teflon impeller stirrer ranging from speeds of 40-60 rpm for this study.

Based on the impeller stirrer design, it is expected that the air flow characteristics inside the chamber at the air-water interface are similar to ambient air, i.e., flow outside the chamber, once steady-state has been reached (Perry and Chilton, 1973). A vent line was fitted to the exiting sample line to prevent pressurization and was periodically bubble tested to check for under pressurization and/or leaks in the enclosed system. The sample exiting the chamber travels through the sample line and is then split in order to deliver the sample simultaneously to the different analysis instruments: a Model 450C pulsed fluorescence H₂S/SO₂ analyzer, and a Model 17C chemiluminescence NH₃ analyzer (Thermo Environmental Corporation, Mountain View, CA).

Multi-point calibrations (80, 60, 40, and 20% of full-range scale) for the Model 450C and Model 17C analyzers were conducted according to the TEI Model 450C and Model 17C instruction manuals prior to each sampling campaign using a TEI Model 146

dilution-titration system (Thermo Environmental Corporation, Mountain View, CA).

During the field study, zero and span checks for H₂S and NH₃-N concentration were conducted daily.

3.2.3 Flux Calculation

In order to calculate NH₃-N and H₂S fluxes for this research experiment, the following mass balance equation was used for the dynamic flow-through chamber system:

$$\frac{dC}{dt} = \left(\frac{q[C_{air}]}{V} + \frac{JA}{V} \right) - (C) \left(\frac{LA_w}{V} + \frac{q}{V} \right) - R \quad (1)$$

where	C	gas concentration inside the chamber
	C_{air}	concentration in carrier air
	q	flow rate of compressed air through the chamber
	V	volume of the chamber
	A	surface area of the lagoon covered by the chamber
	A_w	inner surface area of the chamber of inner and upper wall surfaces
	L	total loss of gas in the chamber per unit area due to reaction with inner and upper walls of the chamber
	h	internal height of the chamber
	J	emission flux per unit area
	R	gas phase reactions inside the chamber

Since zero-grade air was used as the carrier gas, C_{air} was assumed to equal zero and gas phase reactions, R, was also assumed to be zero. Since the air inside the chamber was assumed to be well mixed by the impeller stirrer, C was assumed to be constant within

the chamber. At steady-state conditions, the change of concentration with respect to time $\left(\frac{dC}{dt}\right)$ was zero. Therefore equation (10) can be simplified as:

$$\frac{J}{h} = C_{eq} \left(\frac{LA_w}{V} + \frac{q}{V} \right) \quad (2)$$

Loss term, L , is determined experimentally while equilibrium-state gaseous concentration (C_{eq}), flow rate (q), and chamber dimensions (A_w , V and h) are all measured. Kaplan et al. (1988) has devised a method for calculating loss term by calculating the slope of the plot of $-\ln \left[\frac{C_{eq} - C(t)}{C_{eq} - C_o} \right]$ versus time (t). For this experiment, C_o is the initial equilibrium state gas concentration measured by the chamber system at a constant flow rate ($\text{m}^3 \text{min}^{-1}$). C_{eq} is the measured gas concentration at a second equilibrium state at an increased or reduced flow rate into the chamber system ($\sim 5\text{-}6$ lpm difference). The flow rate for both C_o and C_{eq} was held constant for at least 20 minutes to allow equilibrium state gas concentration to be reached inside the chamber. $C(t)$ depicts gas concentration at any time, t , during the transition between the first and second equilibrium states. L is determined by:

$$L = \left(\text{slope} - \frac{q}{V} \right) \left(\frac{V}{A_w} \right) \quad (3)$$

Upon statistical analysis, for steady-state conditions in the lagoon (i.e., when the flux was not increasing or decreasing significantly with time) it was determined that the loss term for $\text{NH}_3\text{-N}$ flux increases exponentially as ambient temperature, T , ($^{\circ}\text{C}$) increases ($n = 5$, $r^2 = 0.79$). An equation based on a semi-logarithmic relationship was then used throughout the experiment to calculate the loss of $\text{NH}_3\text{-N}$ to the internal chamber walls and was given by:

$$L_{NH_3-N} = 0.0355 * T - 2.5454 \quad (4)$$

Where L_{NH_3-N} is the loss of NH_3-N by the chamber wall per unit area ($m \text{ min}^{-1}$). Loss to the internal chamber wall areas was found to be $< 20\%$ for all seasons. The loss term was not considered for H_2S flux because solubility is much lower and the gas did not exhibit loss to the internal chamber walls.

3.2.4 Meteorological and Lagoon Parameters Instrumentation

A 10 meter meteorological tower was erected to measure ambient wind speed and direction, air temperature, relative humidity, and solar radiation. A Met One Instruments Model 034-B Windset (Campbell Scientific, Inc., Logan, UT) with an integrated cup anemometer and wind vane mounted on a common shaft was used to measure wind speed and direction at 10 m above the surface. Air temperature and relative humidity (RH) measurements were made at 2 m height with a Model CS500-L Vaisala 50Y temperature and RH probe (Campbell Scientific, Inc., Logan, UT) housed in a Model 41303 RM Young 6-plate gill solar radiation shield (Campbell Scientific, Inc., Logan, UT). Solar radiation measurements was also made at 2 meter height (facing south) using a Model LI200X Silicon Pyranometer fixed calibration probe (Campbell Scientific, Inc., Logan, UT).

A Model CSIM11 pH probe (Campbell Scientific Inc., Logan, UT) was used to continuously monitor near-surface lagoon pH. The pH probe was periodically buffer tested to ensure accuracy and calibration curves were established. Two CS107 (Campbell Scientific Inc., Logan, UT) temperature probes simultaneously measured lagoon surface temperatures inside the chamber as well as 0.3 m outside the chamber to ensure there are

no significant differences (see Chapter 1, Section 1.2.4.1). The pH and temperature probes were each submerged in the lagoon at a depth of ~6-7cm beneath the surface.

A Model CR10X data logger equipped with a Model AM 16/32 Channel Relay Multiplexer (Campbell Scientific, Inc., Logan, UT) was used to collect all meteorological and lagoon data and a Model CR23X was used to acquire all gaseous and mass flow data. A Dell Inspiron 600m laptop computer was used to download the data and the time was checked daily on the data loggers to ensure continuity. Data was collected every second, and averaged and recorded over a 15 minute timeframe. The data loggers and gas analyzers were housed inside a temperature-controlled mobile laboratory (N.C. State University Air Quality Ford Aerostar Mini-Van), maintained at ~21°C (~70°F).

3.2.5 Lagoon Sample Collection

Lagoon samples were collected daily between 10:00 and 13:00 during each sampling week using sterile plastic 500mL bottles and submitted to the North Carolina Division of Water Quality (NC DWQ) for total ammoniacal nitrogen (TAN), total Kjeldahl nitrogen (TKN), and total sulfide analysis. Occasionally, samples were also collected during the early morning or late afternoon as well to check for diurnal variations in concentration levels. Samples were collected from the lagoon surface simultaneously at the chamber system and at a randomly chosen location at the lagoon. Lagoon samples collected for TAN and TKN analyses were preserved with sulfuric acid to pH < 2 and samples collected for sulfide analyses were preserved with 6N sodium hydroxide and 2N zinc acetate to pH > 9, according to NC DWQ specifications. All samples were immediately stored on ice (<4°C) and brought to the NC DWQ laboratory within 48 hours for analysis.

3.3 Results

Continuous in situ emissions measurements were made for $\text{NH}_3\text{-N}$ and H_2S for ~1 week during each season (Fall: October 26-November 1, 2004; Winter: February 14-19, 2005; Spring: April 14-18, 2005; Summer: June 14-18, 2005) for a one-year period. Data was not collected during precipitation or other disturbed weather events.

3.3.1 Diurnal and Seasonal Flux

A total of 1231 ($\text{NH}_3\text{-N}$) and 1672 (H_2S) 15-minute averaged concentration values were recorded during the four seasonal experiments. During all seasons, $\text{NH}_3\text{-N}$ flux was 3-4 orders of magnitude greater than H_2S flux from the lagoon. The NH_3 analyzer was set to collect data at the highest concentration range, maximum value of 20 000 parts per billion (ppb). Approximately 23% of the data recorded was above the maximum detectable limit, all during the spring and summer initiatives. Only two 15-minute averaged concentration values within range ($< 20\,000$ ppb) were recorded during the summer. Alternatively, more than 60% of the 15-minute averaged H_2S concentration values were recorded below the minimum detectable limit (1 ppb) and were therefore considered to be negligible. Table 3.1 shows the number of data points that were within and either above (NH_3) or below (H_2S) detectable limits for each analyzer. Knowledge of meteorological and lagoon parameters above and below the range of each gaseous concentration are certainly useful; however, we note that only data recorded within the range for $\text{NH}_3\text{-N}$ was used to perform further analyses.

Table 3.2 summarizes the $\text{NH}_3\text{-N}$ and H_2S fluxes from the lagoon for each season and data were further averaged to demonstrate the daily hourly-averaged flux patterns in Figure 3.4 (a and b). Randomly selected data points provide error bars (one standard

deviation) to show variability in the seasonal measurements. Data gaps in the graphs represent times during the experiment when zero/span checks were being performed on the analyzers and cylinders containing the carrier gas were changed. The lowest average daily fluxes for both H₂S and NH₃-N were observed during the winter experimental period, $\sim 0.0 \mu\text{g m}^{-2} \text{ min}^{-1}$ and $1290 \mu\text{g-N m}^{-2} \text{ min}^{-1}$, respectively. During the winter season, only 2.3% of the H₂S concentration values were above the minimum detectable limit (1 ppb) for the analyzer and so the flux value was considered to be negligible. The highest observed average daily H₂S flux values, $5.3 \mu\text{g m}^{-2} \text{ min}^{-1}$, were observed during the summer. It is of interest to note the unusual diurnal flux pattern observed during this season. Hourly-averaged flux values were highest during the nighttime and lowest during mid-afternoon. Yongsiri et al. (2005) report that at higher pH values (i.e., pH = 8) the increase in liquid temperature causes the molecular H₂S to dissociate to the ionic form bisulfide (HS⁻). However, warmer temperatures are associated with increased biological lagoon activity (U.S. EPA, 2002) and therefore the aqueous sulfide concentrations during summer are higher than other cooler seasons, likely accounting for the generally higher emissions. On the other hand, during the spring the flux maximizes during the mid-to-late afternoon although the values are much lower, $0.5 \mu\text{g m}^{-2} \text{ min}^{-1}$. Generally, almost 87% of the total H₂S flux was observed during the summer season. Results of hydrogen sulfide flux from previous studies are presented in Table 3.3. All are from farms located in the Midwest U.S. All report emissions ~ 2 -3 orders of magnitude greater than results from this study, with the exception of Byler et al. (2004), where summer H₂S flux was estimated to be $4.2 \mu\text{g m}^{-2} \text{ min}^{-1}$ from a phototropic lagoon. Lim et al. (2003) reported much higher H₂S flux values of 546 (pH 7.9-8.2) and 136 (pH 7.3-8.4)

$\mu\text{g m}^{-2} \text{ min}^{-1}$ at two breed-to-wean farms in Illinois and Indiana during spring/summer, collecting 10-minute integrated samples in 50-L Tedlar bags. The time of day when the samples were collected was not reported and no diurnal profiles were provided. There is also no data reported for H_2S or sulfide concentrations in the lagoon. This parameter may account for the flux differences between the two studies. Zahn et al. (2001) made semi-continuous measurements for three seasons at a swine farm in eastern Missouri using a theoretical shape profile (TSP) micrometeorological technique. Average seasonal flux ranged from $438\text{-}1266 \mu\text{g m}^{-2} \text{ min}^{-1}$. The lagoon sulfide content reported in this lagoon was higher compared to this study, likely accounting for some of the increased flux rate.

For $\text{NH}_3\text{-N}$, the concentration exceeded the maximum value (20,000 ppb) on the analyzer during almost the entire summer experiment. The diurnal variation shown in Figure 3.4b has taken into account loss of NH_3 to the chamber walls and so a diurnal profile is pronounced, due to the temperature dependency shown in Equation (4). The average daily flux value of $4294 \mu\text{g-N m}^{-2} \text{ min}^{-1}$ is reported only to demonstrate the dramatic increase during the warmest months and should not be considered a true flux value. For the spring season, no maximum flux values are reported in Table 3.2 because ~29% of 15-minute averaged NH_3 concentration values were above the maximum detectable limit for the analyzer. The average flux reported for this season is also not a true flux value but is shown to simply demonstrate the seasonal dependence on NH_3 flux. The actual flux for both spring and summer is assumed to be higher, but the extent of the increase is unknown.

Results of hydrogen sulfide flux from previous studies are presented in Table 3.4. All studies appear to be within one order of magnitude of each other. Higher pH values,

lagoon TAN concentrations, and seasonal variations may account for some of the differences. Aneja et al. (2006c) measured $\text{NH}_3\text{-N}$ flux in 2002-2003 from the same lagoon used for this study. Results are comparable for the fall experiment; however, measured flux is ~ 3.5 times higher during this study. Zahn et al. (2001) report little variation from their three seasonal measurements with flux ranges of $1080\text{-}1104\ \mu\text{g-N m}^{-2}\ \text{min}^{-1}$. Lim et al. (2003) reported a large variation in flux measurements at two different lagoons measured during the same season. Previously, Aneja et al. (2000) reported a range of ammonia flux values of $305\text{-}4017\ \mu\text{g-N m}^{-2}\ \text{min}^{-1}$ from another hog farm in North Carolina during four seasons and predicted the ammonia flux by an observational model, $\log_{10}(\text{NH}_3\text{-N flux}) = 0.048 \cdot T_L + 2.1$ where T_L is near-surface lagoon temperature in $^{\circ}\text{C}$.

3.3.2 Aqueous Lagoon Concentration

Lagoon samples were collected daily throughout each experimental period at the surface near the experimental chamber system and simultaneously at a randomly chosen location at the lagoon. The samples were compared to check for differences in concentration levels between the fixed chamber location and other random locations where effluent samples were collected. Using SAS Statistical Software Version 8.2 (SAS Institute, Cary, NC), an independent samples t-test was performed ($n = 23$) and it was determined that there was no significant difference ($p\text{-value} > 0.05$) in concentration (mg L^{-1}) for any of the lagoon samples (sulfide, TAN, TKN). It is therefore assumed that the concentration levels are uniform throughout the lagoon surface.

3.3.2.1 Aqueous Sulfide and Hydrogen Sulfide Flux

Aqueous hydrogen sulfide exists in equilibrium with the bisulfide anion (HS^-) and the sulfide anion (S^{2-}) and all three comprise total sulfide. Once total sulfide (C_{TS}) concentration has been determined, the bulk dissolved hydrogen sulfide, which is a function of C_{TS} , pH, and lagoon temperature (T_L), can then be calculated. Snoeyink and Jenkins (1980) determined the relationship for the fraction of sulfide species (H_2S , HS^- , S^{2-}) present in aqueous solution as a function of pH (Figure 3.5) and estimated the aqueous H_2S concentration for known C_{TS} by the following equation:

$$C_{\text{H}_2\text{S}} = C_{\text{TS}} \left(\frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_{a,1}[\text{H}^+] + K_{a,1}K_{a,2}} \right) \quad (5)$$

where $C_{\text{H}_2\text{S}}$ is the concentration of dissolved hydrogen sulfide, $[\text{H}^+]$ is the hydrogen ion concentration (i.e., $10^{-\text{pH}}$), and $K_{a,1}$ and $K_{a,2}$ are the acidity (rate dissociation) constants for H_2S and HS^- , respectively, in the aqueous phase.

The dissociation of molecular H_2S in water increases at pH values above 7 and, as pH shifts from alkaline to acidic ($\text{pH} < 7$), the potential for H_2S emissions increases. The sulfide anion can form at $\text{pH} > 12$, well above the range for a typical hog lagoon, and so it is not expected to be present in the effluent sampled. Only the molecular $\text{H}_2\text{S}_{(\text{aq})}$ fraction, not the ionized form (HS^-), can be transferred across the gas-liquid interface (U.S. EPA, 1974).

Table 3.5 lists simple statistics for the aqueous sulfide concentrations measured during each season. The calculated average dissolved H_2S concentration generally comprised 10-17% of total dissolved sulfide, which ranged from 0.1-13.0 mg L^{-1} . The highest average sulfide concentrations, 9.2 mg L^{-1} , were observed during the summer. The relationship between average daily H_2S flux and lagoon H_2S aqueous concentration

is illustrated in Figure 3.6a and shows generally a linear increase ($r^2 = 0.69$). During the winter, both H_2S flux and aqueous concentration are low, likely due to low temperatures (average 11.5°C) and subsequent low biological activity in the lagoon.

3.3.2.2 TAN and Ammonia Flux

Ammonia (NH_3) and ammonium (NH_4^+) comprise total ammoniacal nitrogen (TAN) and only unionized NH_3 can transfer across the gas liquid interface. The TAN concentration values were ~ 3 -4 orders of magnitude larger than measured sulfide and remained relatively constant during each experiment, ranging from seasonal averages of 378 mg-N L^{-1} in the fall to 568 mg-N L^{-1} in the spring. The amount of NH_3 that comprises TAN is dependent on lagoon temperature and pH and can be calculated based on data from Emerson et al. (1975). Similar to H_2S , the relationship between average daily $\text{NH}_3\text{-N}$ flux and unionized NH_3 aqueous concentration (Figure 3.6b) shows a linear increase ($r^2 = 0.82$). During this study, aqueous NH_3 was approximately 1 to 13% of measured TAN.

3.3.3 Lagoon pH and Flux

Table 3.5 provides average pH values during the different seasonal measurement periods. The results show that there are only slight variations in pH throughout the year. The lowest seasonal average pH, 8.0 ± 0.1 was measured during the summer. Table 3.6 lists the Pearson Correlation Coefficient ($r^2 = 0.61$, $p\text{-value} < 0.0001$) for the 15-minute averaged logarithmic H_2S flux value versus lagoon pH, indicating a negative relationship between H_2S flux and pH, as expected (see Figure 3.5). A semi-logarithmic plot of hourly averaged H_2S flux and pH further demonstrates the relationship (Figure 3.7a).

For the logarithmic value of $\text{NH}_3\text{-N}$ flux, results indicated that only ~4% of the variation could be explained by pH alone ($r^2 = .04$, $p < 0.0001$) (Table 3.4). However, it is important to note that none of the flux values were considered for the correlation calculation when measured $\text{NH}_3\text{-N}$ concentrations exceeded maximum values (20 000 ppb) on the analyzer. When the concentrations were above 20 000 ppb the average lagoon pH was ~8.0, lower than the other three seasons (plotted in Figure 3.7b). It is interesting to notice that $\text{NH}_3\text{-N}$ flux has a negative relationship with pH in this study. It would be expected that, since ammonia is a basic gas, $\text{NH}_3\text{-N}$ flux should increase as pH increases, indicating that other parameters combined (i.e., lagoon temperature and effluent concentration) may have a stronger influence. Also, the variation in pH during all four experiments may be considered small, ranging from 7.9 to 8.2 throughout the year.

3.3.4 Lagoon Temperature and Flux

The average lagoon temperature varied from 11.5°C in the winter to 29.7°C in the summer. The average lagoon temperature when H_2S was measured at concentration levels greater than 1 ppb was 24.0°C; while the average lagoon temperature was much lower (14.5°C) when the concentration was considered negligible (< 1 ppb). This is expected as anaerobic bacteria are ineffective at temperatures below 15°C (U.S. EPA, 2002). The Pearson Correlation Coefficient, r , (Table 3.6) for the 15-minute averaged logarithmic H_2S flux value and lagoon temperature was 0.83, $p < 0.0001$, indicating that ~70% (coefficient of determination, r^2) of the H_2S flux can be explained by the lagoon temperature. The relationship Figure 3.7c shows the positive relationship between these two variables. However, as discussed previously, the lagoon temperature also affects the

biological activity in the lagoon, and the higher activity likely leads to higher aqueous sulfide concentration levels.

For logarithmic $\text{NH}_3\text{-N}$ flux, the correlation with lagoon temperature was strong ($p < 0.0001$), with almost 26% of the variability explained by lagoon temperature. Again, none of the flux values were considered when $\text{NH}_3\text{-N}$ concentrations exceeded maximum values on the analyzer during measurements. At these high values, average lagoon temperatures were 24.9°C . Figure 3.7d provides a graph of the hourly averaged logarithmic $\text{NH}_3\text{-N}$ values plotted against the respective lagoon temperatures. All values, including maximum are shown on the graph simply to illustrate the positive relationship between temperature and flux. It is noted that the loss of ammonia to the internal chamber wall areas (calculated from Equation 4) is also temperature dependent and influences the flux calculation indirectly. The flux during the fall was slightly lower at the same lagoon temperatures as compared to the winter and spring experimental periods. However, it is important to recall that the aqueous TAN lagoon concentration was lower during the fall as opposed to the other seasons ($> 100 \text{ mg L}^{-1}$). Unfortunately, for this study it was not possible to perform a multiple linear regression analysis including effluent concentration because lagoon samples were collected only once (or twice on occasion) per day as compared to all other parameters which are 15-minute averaged continuous measurements.

3.3.5 Meteorological Parameters and Flux

Wind speed was measured at a reference height of 10 m. Utilizing the power law profile, frequently used in air pollution applications (Arya, 1999), wind velocities at 0.1m

(the height of the impeller stirrer in the chamber) were estimated. The power law profile is given by

$$\frac{V}{V_r} = \left(\frac{z}{z_r} \right)^m \quad (8)$$

where V_r is the wind velocity at reference height z_r and m is given as 0.15 for water surfaces (Arya, 1999). The dynamic flow through chamber system utilizes a continuous impeller stirrer to ensure a well-mixed region inside the chamber and meets the criteria for performance as a Continuously Stirred Tank Reactor (CSTR). Aneja et al. (2000) provide more detailed information regarding the CSTR and also measured the wind speeds inside a similar chamber system. The study observed wind speeds ranging from ~ 1.0 - 2.5 ms^{-1} , dependent on the speed set on the stirrer. In this study, average wind speeds at a height 0.1m above the lagoon surface were $\sim 1.8 \text{ ms}^{-1}$.

Ambient temperature was positively correlated with logarithmic H_2S flux ($r^2 = 0.43$, $p < 0.0001$) while wind speed showed a negative and much lower correlation ($r^2 = 0.02$, $p < 0.0001$) (Table 3.6). Arogo et al. (1999) performed a laboratory study and determined a slight decrease in the H_2S mass transfer coefficient in aqueous solution as air velocity increased. Those results corroborated the observation by Whitman (1924) that wind speed above the surface will have a small effect on emissions of a relatively insoluble gas across the gas-liquid interface.

For $\text{NH}_3\text{-N}$, emissions were positively correlated with ambient temperature and wind speed ($r^2 = 0.15$ and 0.11), respectively, while relative humidity was negatively correlated, $r^2 = 0.34$. All correlations were statistically strong ($p < 0.0001$); however the relationship between each of the variables may be considered practically weak.

It should be noted that the chamber system cannot completely simulate climatic conditions (i.e., wind, air temperature, solar radiation, atmospheric stability effects) and therefore the above correlations may not be representative of correlations in the ambient environment (Aneja et al., 2006b; Arogo et al., 2003). However, the chamber technique has the important advantage of association of a particular emission site and its measurable array of physical, chemical, and microbiological properties with emissions of particular compounds or their reaction products (Aneja et al., 2006b).

3.4 Conclusions

Emissions of atmospheric ammonia-nitrogen and hydrogen sulfide from a commercial anaerobic swine waste treatment lagoon were measured over a one year period during four different seasons in an effort to examine diurnal and seasonal variability and the respective relationships of $\text{NH}_3\text{-N}$ and H_2S emissions to lagoon physicochemical properties and meteorological parameters. For $\text{NH}_3\text{-N}$, the largest fluxes were observed during the summer ($> \sim 4200 \mu\text{g N m}^{-2} \text{ min}^{-1}$). During the fall and spring, average $\text{NH}_3\text{-N}$ fluxes were 1634 ± 505 and $> 2495 \mu\text{g N m}^{-2} \text{ min}^{-1}$, respectively. The lowest fluxes were observed during the winter where average flux values were $1290 \pm 246 \mu\text{g N m}^{-2} \text{ min}^{-1}$. The lowest fluxes for H_2S were also observed during the winter season, $\sim 0.0 \mu\text{g m}^{-2} \text{ min}^{-1}$. Average fluxes increased during the fall ($0.3 \pm 0.1 \mu\text{g m}^{-2} \text{ min}^{-1}$) and spring (0.5 ± 1.0) and were observed at highest flux values during the summer ($5.3 \pm 3.2 \mu\text{g m}^{-2} \text{ min}^{-1}$). Generally, the lagoon emissions for H_2S were $\sim 3\text{-}4$ orders of magnitude less than $\text{NH}_3\text{-N}$ during all four measurement periods.

Hydrogen sulfide emissions were well correlated with lagoon aqueous H_2S concentration, lagoon temperature, and pH. Based on the dynamic-flow through chamber

technique, ambient meteorological parameters, including wind speed and relative humidity, appeared to have much smaller influences over emission rates. Emissions of $\text{NH}_3\text{-N}$ were influenced primarily by lagoon TAN measurements as well as lagoon temperature; however, in this study pH showed a slight negative correlation with $\text{NH}_3\text{-N}$ flux. For ambient meteorological parameters, relative humidity was observed to have a somewhat moderate negative correlation with $\text{NH}_3\text{-N}$. However, the chamber technique may not accurately simulate ambient environment conditions.

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Table 3.1. Number of data points (n) that were within and out of range for each analyzer. Each data point represents a 15-minute concentration average recorded from analog output from the respective analyzer. The NH₃ analyzer has a maximum range of 20,000 part per billion (ppb) and the H₂S has a minimum detectable limit of 1.0 ppb.

	Fall Oct 26-Nov 1, 2004	Winter Feb 15-21, 2005	Spring Apr 14-19, 2005	Summer Jun 14-18, 2005	Total
NH ₃					
n (ppb < 20 000)	311	387	250	2	950
n (ppb > 20 000)	0	0	101	180	281
Total n	311	387	351	182	1231
H ₂ S					
n (ppb > 1.0)	141	11	153	362	667
n (ppb < 1.0)	341	466	198	0	1005
Total n	482	477	351	362	1672

Table 3.2. Statistical summary table of average daily NH₃-N and H₂S fluxes for each season

Season	Mean ^a	Minimum	Maximum
NH ₃ -N Flux ^b			
Fall 2004	1634(505)	1110	3305
Winter 2005	1290(246)	867	2027
Spring 2005	> 2495 ^c	1565	NA
Summer 2005	> 4294 ^d	3864	NA
H ₂ S Flux ^b			
Fall 2004	0.3(0.1)	0.0	0.8
Winter 2005	~0.0(0.2)	0.0	1.2
Spring 2005	0.5(1.0)	0.1	7.1
Summer 2005	5.3(3.2)	0.8	13.3

NH₃-N flux = (14/17) NH₃ flux

^a Numbers in parenthesis represent one standard deviation

^b Units of flux are µg m⁻² min⁻¹

^c NH₃ concentration was above maximum range on the ammonia analyzer for 29% of 15-minute averaged data; maximum and average flux values are unknown.

^d NH₃ concentration was above maximum range on the ammonia analyzer for 99% of 15-minute averaged data; maximum and average flux values are unknown.

Table 3.3. Lagoon hydrogen sulfide fluxes from previous studies compared with this study.

<i>Researcher</i>	<i>Season</i>	<i>Experimental Method</i>	<i>Lagoon Size m²</i>	<i>Lagoon Temperature °C</i>	<i>pH</i>	<i>Sulfide Concentration mg L⁻¹</i>	<i>H₂S Emissions µg m⁻²min⁻¹</i>
Zahn et al. (2001)	August	Theoretical Shape Profile		-	8.1	15 ± 2	438 ± 24
Zahn et al. (2001)	September	Theoretical Shape Profile		-	8.2	17 ± 3	492 ± 24
Zahn et al. (2001)	October	Theoretical Shape Profile		-	8.1	18 ± 1	1266 ± 36
Lim et al. (2003)	April-July	Tedlar bag collection via BCFC ^a	30 735	25	8.1	-	546 ± 96
Lim et al. (2003)	April-July	Tedlar bag collection via BCFC ^a	12 310	25	7.9	-	138 ± 192
Byler et al. (2004) ^b	May-June	Wind tunnel / Jerome meter		-	7.8	-	114 ^c
Byler et al. (2004) ^b	May-June	Wind tunnel / Jerome meter		-	7.4	-	192 ^d
Byler et al. (2004) ^b	July-August	Wind tunnel / Jerome meter		-	8.1	-	4.2 ^c
Byler et al. (2004) ^b	July-August	Wind tunnel / Jerome meter		-	7.7	-	19.2 ^d
This study	October-November	Dynamic Flow-Through Chamber	30 630	18	8.1	0.6 ± 0.4	0.3 ± 0.1
This study	February	Dynamic Flow-Through Chamber	30 630	12	8.1	3.2 ± 3.3	~0.0
This study	April	Dynamic Flow-Through Chamber	30 630	15	8.1	1.8 ± 0.6	0.5 ± 1.0
<i>This study</i>	June	Dynamic Flow-Through Chamber	30 630	30	8.0	9.2 ± 2.5	5.3 ± 3.2

^a Buoyant Convective Flux Chamber^b Average value from three lagoons^c Measured from phototropic lagoon^d Measured from non-phototropic lagoon

Table 3.4. Lagoon ammonia fluxes from previous studies compared with this study.

<i>Researcher</i>	<i>Season</i>	<i>Lagoon Size m²</i>	<i>Lagoon Temperature °C</i>	<i>pH</i>	<i>TAN Concentration mg L⁻¹</i>	<i>NH₃-N Emissions µg m⁻²min⁻¹</i>
Zahn et al. (2001)	August	7 800	-	8.1	917 ± 12	1080 ± 36
Zahn et al. (2001)	September	7 800	-	8.2	934 ± 8	1104 ± 18
Zahn et al. (2001)	October	7 800	-	8.1	929 ± 7	1104 ± 24
Lim et al. (2003)	April-July	30 735	25	8.1	2058	7264 ± 1384
Lim et al. (2003)	April-July	12 310	25	7.9	814	2718 ± 1482
Aneja et al. (2000)	August		30	7.5	648 ± 28 ^b	4017 ± 987
Aneja et al. (2000)	December		12	8.0	663 ± 34 ^b	844 ± 401
Aneja et al. (2000)	February		12	7.8	642 ± 39 ^b	305 ± 154
Aneja et al. (2000)	May		25	7.7	603 ± 48 ^b	1706 ± 552
Aneja et al. (2006c)	September	15 170	27	8.1	442 ± 28	2345 ± 986
Aneja et al. (2006c)	January	15 170	7	8.4	560 ± 19	153 ± 52
Aneja et al. (2006c) ^c	October	30 630	25	8.2	364 ± 36	1685 ± 516
Aneja et al. (2006c) ^c	January-February	30 630	7	8.1	636 ± 37	370 ± 147
This study	October-November	30 630	18	8.1	378 ± 12	1634 ± 505
This study	February	30 630	12	8.1	489 ± 15	1290 ± 246

^a Buoyant Convective Flux Chamber

^b Total Klejdahl nitrogen (TKN) reported

^c Same lagoon as this study (measured in 2002-2003)

Table 3.5. Sampling periods for NH₃-N and H₂S lagoon flux experiments and simple statistics (mean, standard deviation, and range) of hourly averaged lagoon surface (~6-7 cm depth) parameters measured during the flux experiments and effluent samples collected at least once per day.

Season	Sample Dates	Lagoon Temperature ^a	Lagoon pH	TAN ^b	TKN-N ^b	Sulfide ^b
Fall	Oct 26 – Nov 1, 2004	18.2(1.7)	8.1 (~0.0)	378(12)	411(11)	0.6(0.4)
		15.7-23.3	8.0 -8.2	360-390 <i>n</i> = 9 ^c	400-430 <i>n</i> = 9 ^c	0.3-1.5 <i>n</i> = 9 ^c
Winter	Feb 15-21, 2005	11.5(1.4)	8.1 (~0.0)	489(15)	536(15)	3.2(3.3)
		9.1-14.5	8.0 -8.2	470-510 <i>n</i> = 8 ^c	520-560 <i>n</i> = 8 ^c	0.1-9.4 <i>n</i> = 8 ^c
Spring	Apr 14-19, 2005	15.1(1.7)	8.1 (~0.0)	568(13)	613(8)	1.8(0.6)
		12.4-19.8	8.0 -8.2	550-590 <i>n</i> = 6 ^c	600-620 <i>n</i> = 6 ^c	1.0-2.5 <i>n</i> = 6 ^c
Summer	Jun 14-18, 2005	29.7(1.4)	8.0 (0.1)	534(22)	578(53)	9.2(2.5)
		26.9-32.5	7.9 -8.1	520-570 <i>n</i> = 5 ^c	540-650 <i>n</i> = 5 ^c	6.4-13.0 <i>n</i> = 5 ^c

^a Measured in units of °Celsius

^b Measured in units of mg L⁻¹

^c *n* = number of samples collected during each sampling initiative

Table 3.6. Pearson correlation coefficients for the log linear relationship between H₂S and NH₃-N flux, and some measured meteorological and lagoon parameters. Each n represents a 15-minute averaged value.

Parameter	<i>Pearson's Correlation Coefficient</i>				
	Ambient Temperature	Lagoon Temperature	Relative Humidity	Wind Speed	pH
Log ₁₀ H ₂ S Flux (n= 1386)	0.65 ^a	0.83	0.03	-0.14	-0.78
	0.43 ^b	0.69	~0.0	0.02	0.60
	p < 0.0001 ^c	p < 0.0001	p = 0.22	p < 0.0001	p < 0.0001
Log ₁₀ NH ₃ -N Flux (n = 1050)	0.38	0.51	-0.58	0.32	-0.21
	0.15	0.26	0.34	0.11	0.04
	p < 0.0001	p < 0.0001	p < 0.0001	p < 0.0001	p < 0.0001

^a Correlation coefficient (r): measure of the strength of the relationship between two variables.

^b Coefficient of Determination (r²): percent of variation that can be explained by the predictor variable

^c p-value: measure of probability that result occurred strictly by chance.

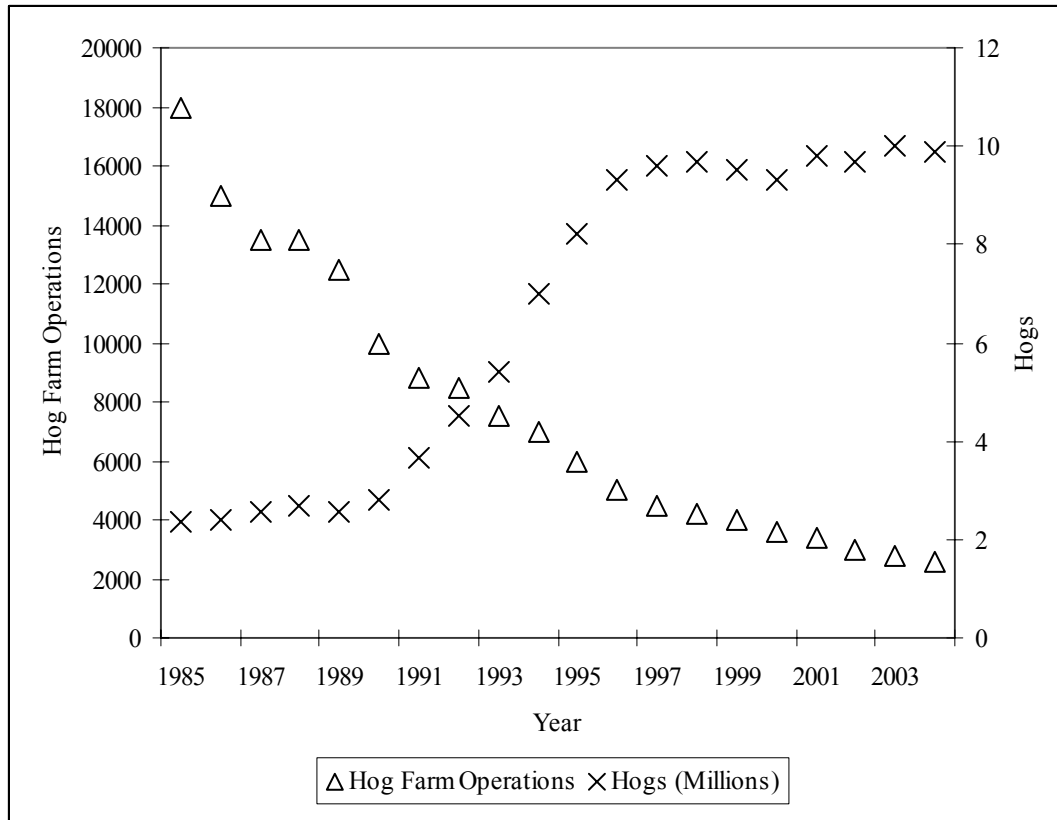


Figure 3.1. Number of North Carolina hog farming operations and hogs from 1985 to 2004.

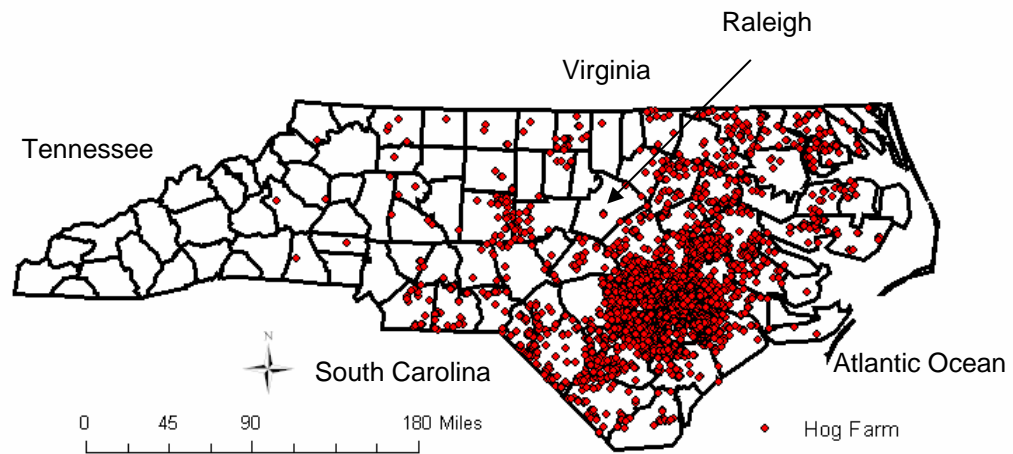


Figure 3.2. Hog farm locations in North Carolina.

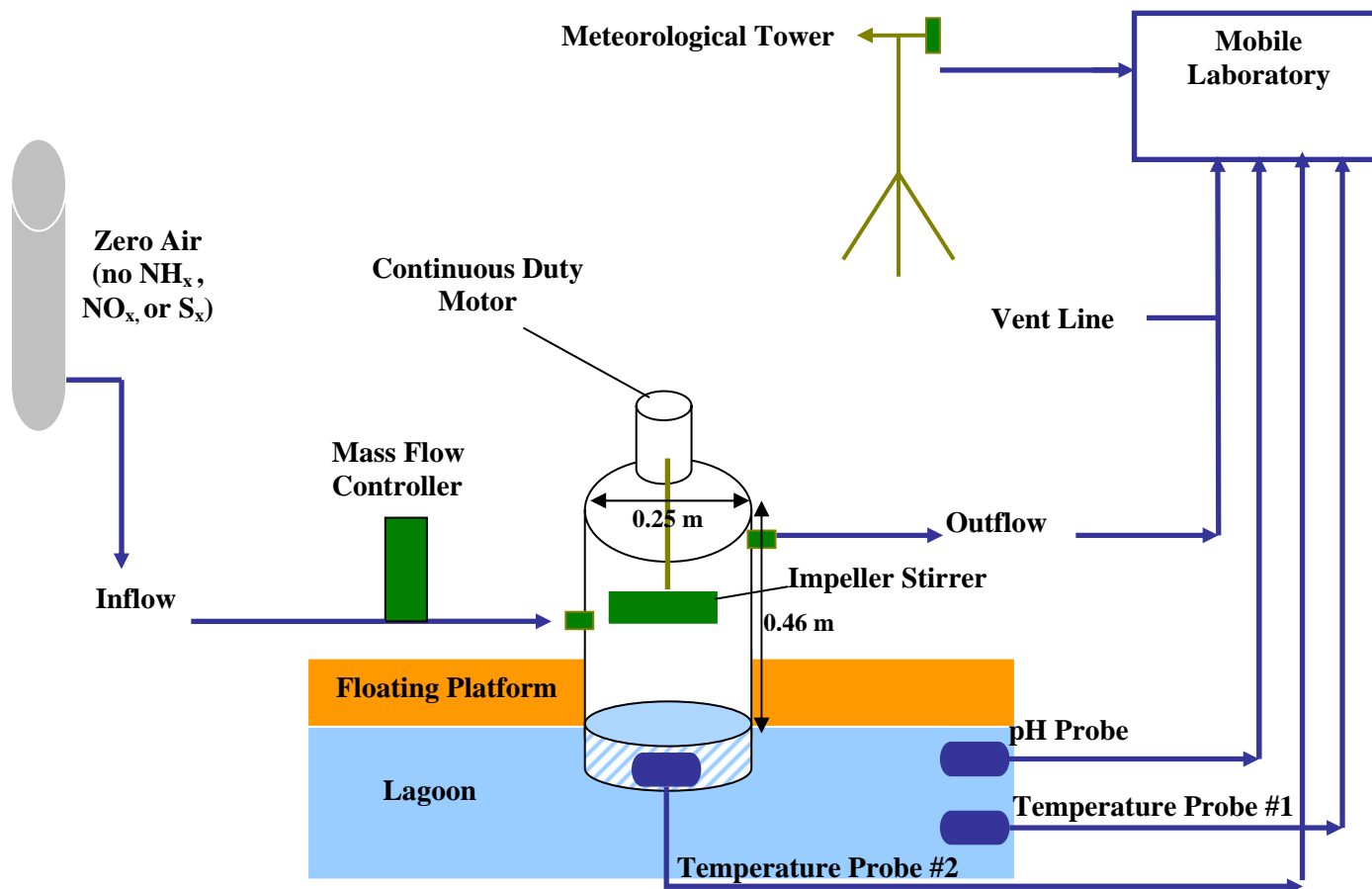
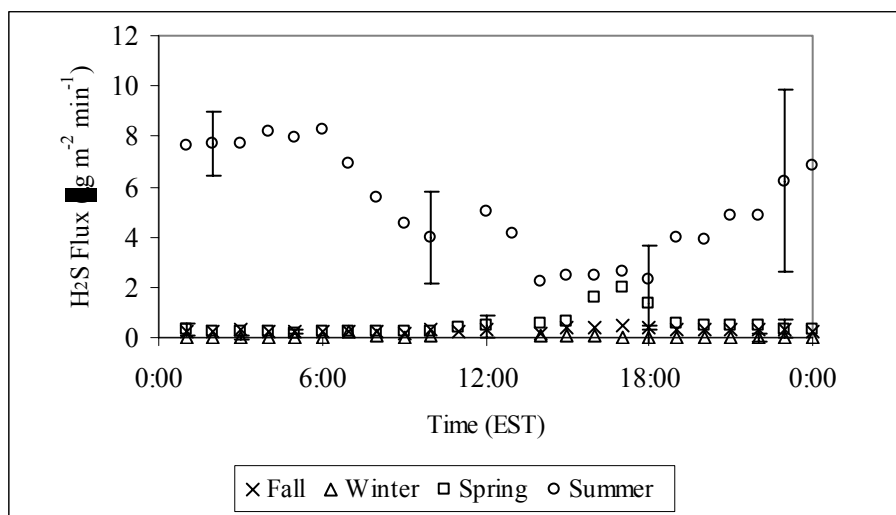
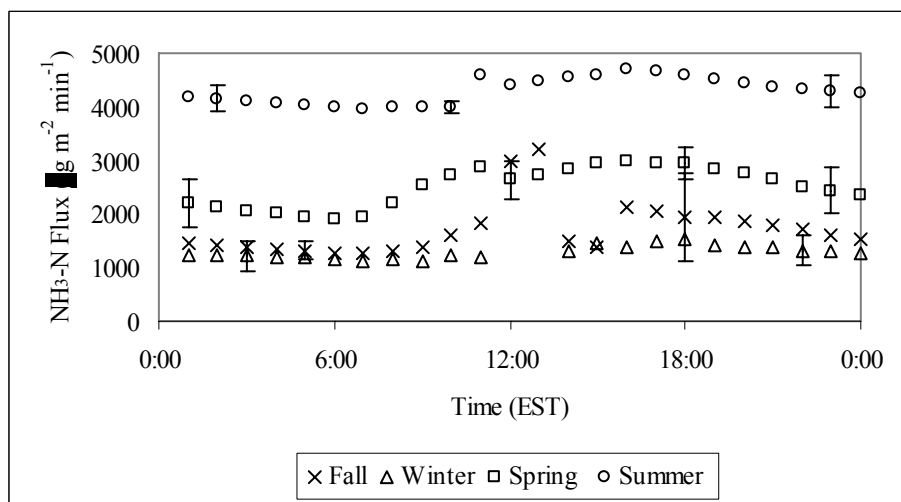


Figure 3.3. Schematic of dynamic flow-through chamber system configured to measure emissions from a swine waste treatment lagoon



(a)



(b)

Figure 3.4. Seasonally averaged diurnal variations of hydrogen sulfide, H_2S , (a) and ammonia, $\text{NH}_3\text{-N}$ (b) flux from anaerobic waste treatment storage lagoon. n (number of days averaged per season) = 6 in fall, $n = 5$ in winter, $n = 5$ in spring, and $n = 5$ and 3 for H_2S and $\text{NH}_3\text{-N}$, respectively, in summer. Spring and summer fluxes are shown to examine differences between seasons although the true flux values are assumed to be higher.

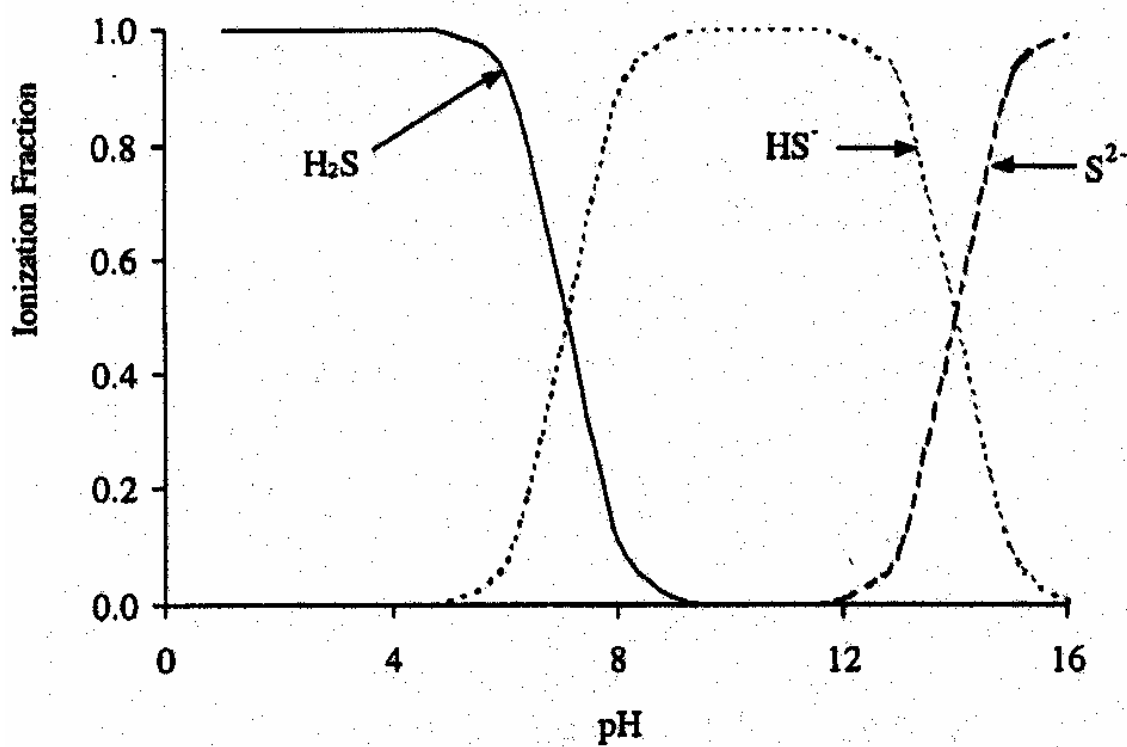


Figure 3.5. Fractions of sulfide species (H_2S , HS^- , S^{2-}) present in aqueous solution as function of pH at 25°C [Source: Snoeyink and Jenkins (1980)]

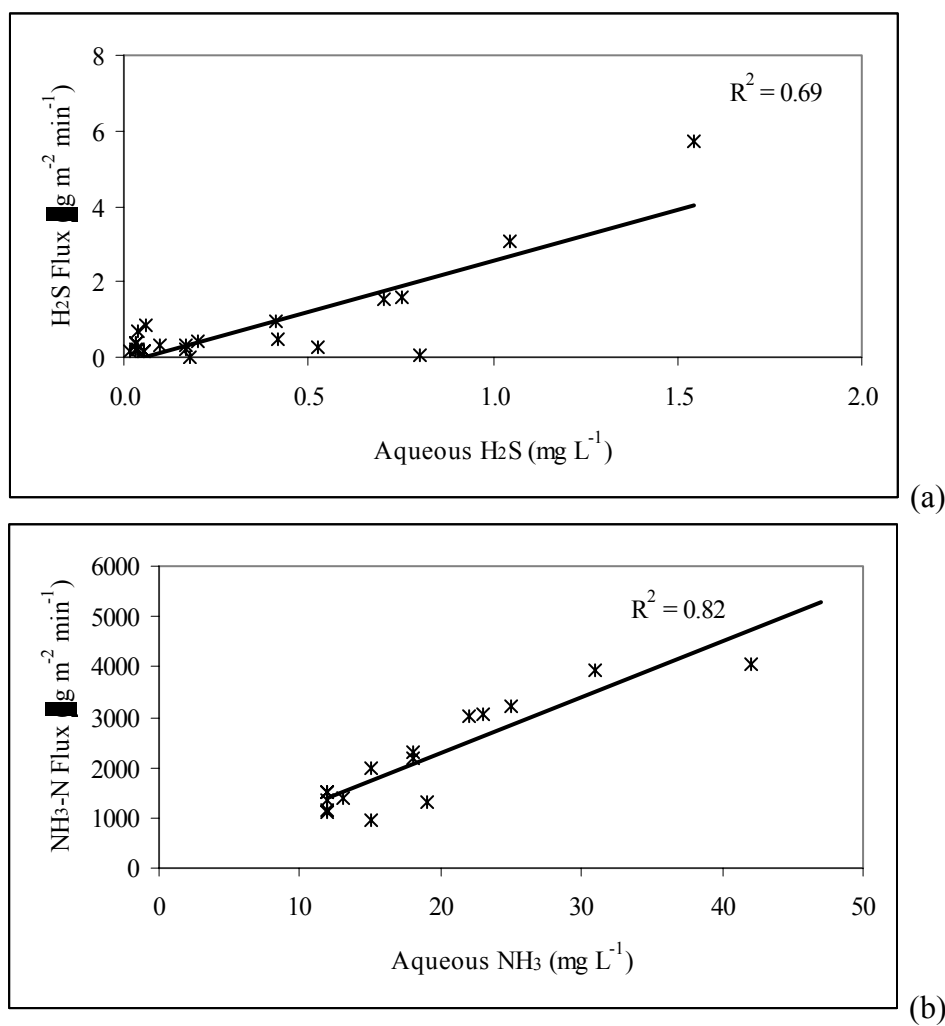


Figure 3.6. Average daily (a) H₂S flux and (b) NH₃-N flux from lagoon surface plotted against respective aqueous concentrations sampled from lagoon on same day as measurements.

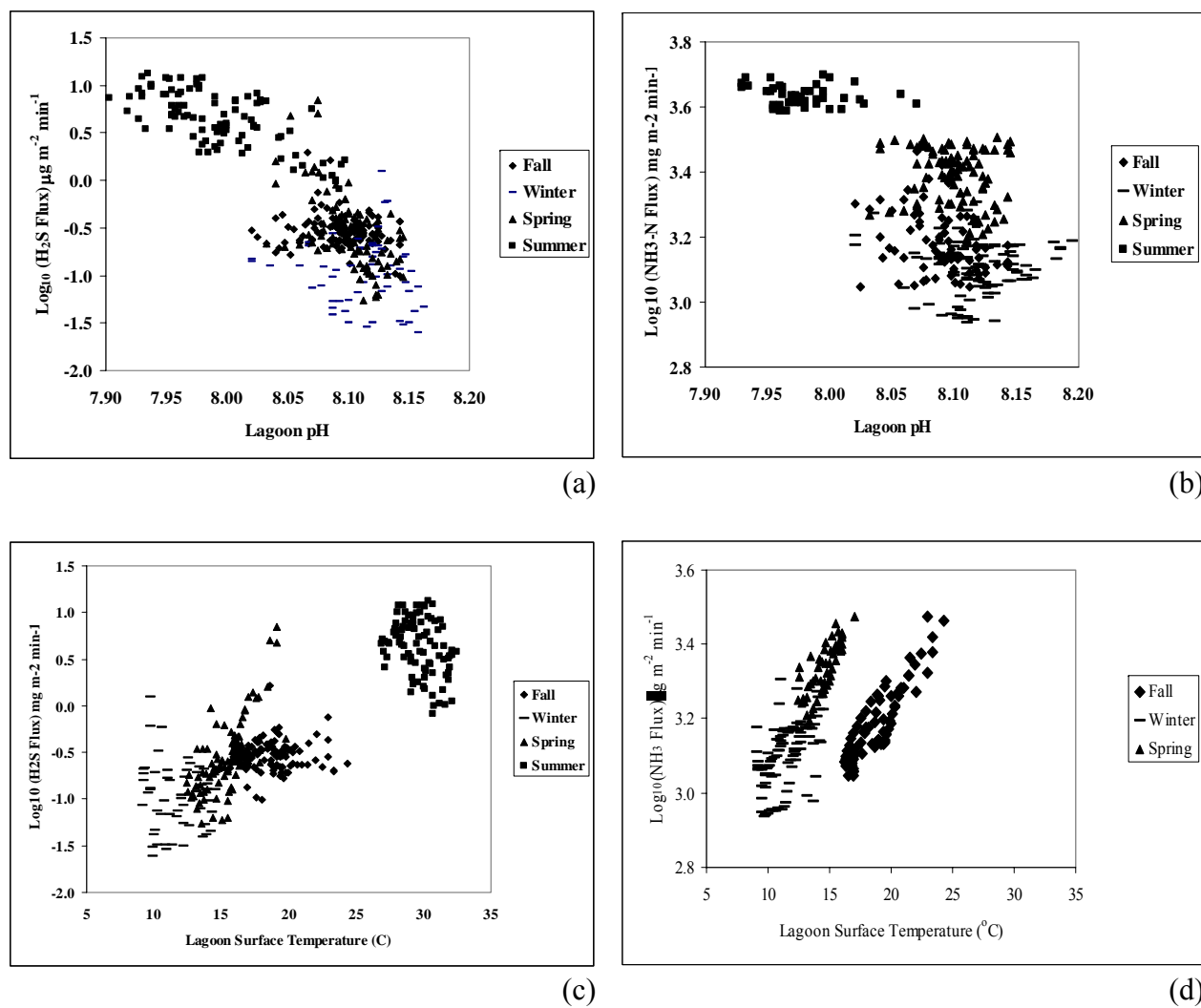


Figure 3.7. Hourly averaged values for lagoon pH versus H_2S flux (a) and $\text{NH}_3\text{-N}$ flux (b) and hourly averaged values for lagoon surface temperature versus H_2S flux (c) and $\text{NH}_3\text{-N}$ flux (d). Only NH_3 measured below detectable limits is provided for 3.7(d).

CHAPTER IV. MODELING HYDROGEN SULFIDE EMISSIONS ACROSS THE GAS-LIQUID INTERFACE OF AN ANAEROBIC WASTE TREATMENT STORAGE SYSTEM

Abstract

Hydrogen sulfide (H_2S) 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 high concentrations. In the southeastern U.S., 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 H_2S emissions from anaerobic waste treatment lagoons is investigated using the coupled Mass Transfer with Chemical Reactions Model (MTCR) with three different assumptions: (1) pH remains constant in the liquid film (MTCR Model I); (2) pH may change throughout the liquid film due to diffusion processes that occur within the film (MTCR Model II); and (3) a simpler Mass Transfer Model which neglects chemical reactions (MTNCR Model).

Results of model predictions indicate that flux is primarily dependent on the physico-chemical lagoon properties including sulfide concentration, pH, and lagoon temperature. Based on mechanistic and empirical equations used in the model, low wind velocities (i.e., $U_{10} < 3.25 \text{ m s}^{-1}$) and air temperature have little 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 H_2S flux is driven by liquid-phase parameters. Model results were compared with H_2S flux measurements made at a swine waste treatment storage lagoon in North Carolina using a dynamic emission flux chamber system in order to evaluate the model's accuracy in

calculating lagoon H_2S 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 qualitative agreement in diurnal comparison (i.e., predicting flux patterns as meteorological and lagoon conditions varied throughout the day) 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 predicted 3-35 times the measured values and both MTCR Models predicted 20-125 times the measured values.

4.1 Introduction

Hydrogen sulfide (H_2S) is a colorless, potentially harmful gas released from swine manure (U.S.EPA, 2001). It is produced as manure decomposes anaerobically, resulting from the mineralization of organic sulfur compounds as well as the reduction of oxidized inorganic sulfur compounds such as sulfate by sulfur-reducing bacteria (U.S. EPA, 2001). The U.S. Center for Disease Control (CDC) warns that brief exposures to concentrations greater than 500 ppm can cause unconsciousness or death (ATSDR, 2004). With a low odor threshold ranging from 0.0005 to 0.3 ppm (ATSDR, 2004), it is also one of the gases released from swine facilities that is associated with odor complaints due to its characteristic “rotten egg” smell.

Once released into the atmosphere, hydrogen sulfide reacts with the hydroxyl radical, OH, oxidizing to form sulfur dioxide (SO_2). Sulfur dioxide then undergoes a series of photochemical reactions, and may eventually form sulfuric acid (H_2SO_4). Sulfuric acid is very hygroscopic, absorbing significant amounts of water at extremely low relative humidities (Seinfeld and Pandis, 1998). As SO_2 is oxidized to H_2SO_4 , the H_2SO_4 formed may undergo heteromolecular nucleation with water vapor (H_2O) to form new H_2SO_4 - H_2O particles or, in the presence of foreign particles, deposit onto preexisting particles (Seinfeld and Pandis, 1998). For locations with low ammonia (NH_3) availability, sulfuric acid exists in the aerosol phase as H_2SO_4 . As the availability of NH_3 increases, H_2SO_4 is converted to HSO_4^- and its salts, and if there is an abundance of NH_3 , to SO_4^{2-} and its salts (Seinfeld and Pandis, 1998). Aerosols such as ammonium sulfate may transport and deposit downwind of its source, possibly leading to nitrogen overloading and other associated environmental problems such as enhanced eutrophication in

sensitive river/coastal ecosystems and soil acidification, which may in turn upset plant nutrient balances near sources (Paerl, 1997).

To date, few studies have reported of H₂S emissions from waste storage treatment lagoons (Zahn et al., 2001; Lim et al., 2003). Arogo et al. (2000) studied the concentration and production of H₂S from stored liquid 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) and developed an overall mass transfer coefficient for emission of H₂S from liquid swine manure.

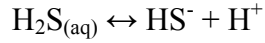
Over the last few years, changes in livestock production methods in the U.S. have led to the emergence of large-scale commercial livestock operations, substantially increasing the number of animals in geographically concentrated areas (Aneja et al., 2006). As emissions of trace gases (i.e., nitrogen and sulfur species) likely increase in parallel with the growth and consolidation of this industry (i.e., more animals confined to fewer farms), it is important to ensure that these operations do not exceed state regulatory ambient levels for gases such as H₂S. Since no H₂S federal standards currently exist, several states have set their own accepted ambient levels (AALs). For example, the 24-hour AAL in North Carolina is 83 ppb (120 µg m⁻³) (Rule 15A NCAC 2D.1104) and the one-hour standard for California is 30 ppb (42 µg m⁻³) (California Air Resources Board). Minnesota's standard is a 30-minute average of 30 parts per billion twice in five days, or a 30-minute average of 50 parts per billion (70 µg m⁻³) twice per year (Minnesota State Air Rules Chapter 7009.0080).

A two-layer film model of gas-liquid interchange between bulk air and bulk water (Figure 4.1) is used to predict H_2S 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 main body of each fluid is assumed to be well mixed and the main resistance to mass transfer across the interface is from the gas and liquid phase interfacial layers where transport occurs by molecular processes. 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). In this study, three process-based models have been developed in order to predict the rates of H_2S emissions from swine waste storage and treatment lagoons. One model considers only diffusion in the two-layer region, neglecting chemical reactions (MTNCR Model). Two coupled Mass Transfer and Chemical Reactions Models based on the concept of simultaneous mass transfer and equilibrium chemical reaction were also developed based on the work done by Olander (1960). One model considers emissions based on the assumption of constant pH throughout the liquid film (MTCR Model I) and the other model considers a possible pH gradient in the liquid film due to diffusion processes (MTCR Model II). Field experiments to measure H_2S emissions from an anaerobic waste treatment lagoon were previously conducted at a commercial swine finishing operation in North Carolina over four predominant seasons (see Chapter 3). These experimental results are used to evaluate the model's accuracy in calculating lagoon H_2S emissions.

4.2 Hydrogen Sulfide in Gas and Liquid Phases

4.2.1 Chemical Reactions in Aqueous Solution

In the liquid phase, molecular H_2S exists in equilibrium with the bisulfide ion (HS^-) and the sulfide anion (S^{2-}). All three comprise total sulfide and are related by the following equilibrium equations:



Once total sulfide (C_{TS}) concentration has been determined, the bulk dissolved H_2S , HS^- , and S^{2-} , which are functions of C_{TS} , pH, and lagoon temperature (T_L), can then be calculated. Snoeyink and Jenkins (1980) determined the relationship for the fraction of sulfide species (H_2S , HS^- , S^{2-}) present in aqueous solution as a function of pH and estimated the aqueous H_2S concentration for known C_{TS} by the following equations:

$$C_{H_2S} = C_{TS} \left(\frac{[H^+]^2}{[H^+]^2 + K_{a,1}[H^+] + K_{a,1}K_{a,2}} \right) \quad (1)$$

$$C_{HS^-} = C_{TS} \left(\frac{K_{a,1}[H^+]}{[H^+]^2 + K_{a,1}[H^+] + K_{a,1}K_{a,2}} \right) \quad (2)$$

$$C_{S^{2-}} = C_{TS} \left(\frac{K_{a,1}K_{a,2}}{[H^+]^2 + K_{a,1}[H^+] + K_{a,1}K_{a,2}} \right) \quad (3)$$

where C_{H_2S} , C_{HS^-} , and $C_{S^{2-}}$ are the concentrations of dissolved hydrogen sulfide, bisulfide ion, and sulfide anion, respectively, $[H^+]$ is the hydrogen ion concentration (i.e., 10^{-pH}), and $K_{a,1}$ and $K_{a,2}$ are the acidity (rate dissociation) constants for H_2S and HS^- , respectively, in the aqueous phase. At $25^\circ C$, $K_{a,1}$ is 1.26×10^{-7} and $K_{a,2}$ is 1×10^{-14} (NRC, 2003). Figure 4.2 shows that the dissociation of molecular H_2S in water increases at pH values above 7, and as pH shifts from alkaline to acidic ($pH < 7$) the potential for

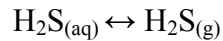
H₂S emissions increases. The sulfide anion can form at pH > 12, well above the range for a typical hog lagoon, and therefore is not considered for this modeling exercise. The acidity constants for H₂S and HS⁻ are functions of temperature. This temperature dependence is based on the Van't Hoff relationship and respective standard enthalpy values (Snoeyink and Jenkins, 1980), and is given by:

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad (4)$$

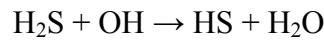
Where K_1 (mol L⁻¹) is the equilibrium constant at temperature T_1 (°K) and K_2 is the equilibrium constant at temperature T_2 , ΔH° (J mol⁻¹) is the enthalpy change, and R is the universal gas constant (J K⁻¹ mol⁻¹). It is important to note that only the molecular H₂S_(aq) fraction, not the ionized forms (HS⁻ and S⁼), can be transferred across the gas-liquid interface (U.S. EPA, 1974).

4.2.2 Chemical Reactions in the Atmosphere

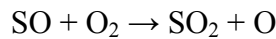
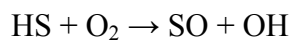
For the physicochemical process of H₂S transfer across the gas-liquid interface, the transfer from the aqueous phase H₂S_(aq) into the gaseous phase H₂S_(g) may be expressed by:



In the gas phase, the only reaction of hydrogen sulfide considered is the reaction with the hydroxyl radical [OH] (Seinfeld and Pandis, 1998):



where HS is eventually oxidized to SO₂,



For this modeling exercise we are concerned strictly with the loss of H₂S and therefore only the chemical reaction for H₂S and OH is considered.

In the gas film, [OH] is assumed to have a constant concentration with an effective first order reaction rate for hydrogen sulfide, providing the following relationship:

$$\frac{d[H_2S]}{dt} = k[OH][H_2S] \quad (5)$$

where k is the temperature dependent rate coefficient for this reaction, calculated by the Arrhenius equation, $k = 6.30 \times 10^{-12} * e^{-80/(273.15+T_a)}$ cm³ molecule⁻¹ s⁻¹ (Jacobson, 1999), where T_a is the air temperature (°C).

The reaction rate constant, k_{ra} , of H₂S in the gas phase is inferred by:

$$k_{ra} = k[OH] \quad (6)$$

where [OH] is the average number of molecules cm⁻³ in the ambient air. For this work, an average value of 5×10^6 molecules cm⁻³ was used, based on values provided by Seinfeld and Pandis (1998); it is noted that OH concentrations may vary widely over time of day, location, and season.

4.3 Coupled Transport with Chemical Reaction Models for Atmospheric Hydrogen Sulfide Emission

4.3.1 Two-Layer Film Theory of Mass Transfer with Chemical Reactions

The principal characteristic of this transport model is the two-layer film model of molecular exchange of gases between water and air (Whitman, 1923; Dankwerts, 1970; Liss and Slater, 1974). Figure 4.1 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 lagoon and the atmosphere. All resistance to mass transport across the interface is due to the layer in which transport occurs by molecular processes.

Generally, the reaction rate for the chemical reactions in the liquid and gas phase will depend on the local concentration of the gas, other reactants with which it reacts, and other physical factors such as temperature and pH. The H_2S concentrations in the bulk liquid and gas phases, C_L and C_a , respectively, are considered constant (since the bulk is assumed to be well mixed). It is noted that there may be uncertainties associated with values (i.e. rate constants, diffusivities) published in literature from various studies.

The general equation of mass transfer with chemical reactions is as follows:

$$D_i \left(\frac{d^2 C}{dz^2} \right) = k_{ri} \times [C] \quad \text{for } k_{ri} > 0 \quad (7)$$

where the diffusion (D_i) of the gas through the film is equal to losses/gains due to chemical reaction (k_{ri}). For the air film, $D_i = D_a$ and $k_{ri} = k_{ra}$, respectively. In the gas phase, zero order and first order reactions may be considered and in the liquid film, zero, 1st, and 2nd order reactions may be considered. The mass transfer model for $k_{ri} = 0$ (i.e., no chemical reactions) will be discussed in Section 4.4.

4.3.2 Mass Transfer in the Gas Film

For the gas film, the basic diffusion equation for 1st order chemical reactions is a second order differential equation whose general solution given by:

$$C(z) = Ae^{r \times z} + Be^{-r \times z} \quad (8)$$

where $r_a = \sqrt{\frac{k_{ra}}{D_a}}$; k_{ra} is an overall rate constant for hydrogen sulfide reaction in the air

and D_a is the diffusivity of hydrogen sulfide in the air. For $k_{ra} = 0$ (i.e., no chemical reactions), the condition will be given later.

Boundary conditions are given as follows:

$$\text{At } z = 0; C_a(0) = C_{ai}$$

$$\text{At } z = t_a; C_a(t_a) = C_a$$

where C_{ai} and C_a is the concentration of hydrogen sulfide at the air-liquid interface and in the bulk gas phase, respectively. Applying these boundary conditions, the following solution may be derived:

$$C(z) = \frac{C_a \left(e^{r_a z} - e^{-r_a z} \right) - C_{ai} \left(e^{(z-t_a)r_a} - e^{-(z-t_a)r_a} \right)}{e^{r_a t_a} - e^{-r_a t_a}} \quad \text{for } 0 < z \leq t_a \quad (9)$$

We will now develop an expression for the flux at the top of the gas film as related to the properties of the gas film and the liquid film concentration at the air-liquid interface.

For the liquid phase, boundary conditions are given as follows:

$$\text{At } z = 0; C_L(0) = C_L$$

$$\text{At } z = t_L; C_L(t_L) = C_{Li}$$

where C_L and C_{Li} is the concentration of hydrogen sulfide in the bulk liquid phase and at the air-liquid interface, respectively. At the interface the gas and liquid fluxes are equal for the conditions, $z = t_L$ for liquid and $z = 0$ for air:

$$J_{Li} = -D_L \left(\frac{dC}{dz} \right)_{(0,t_L)} \quad \text{at } z = t_L \text{ in the liquid phase} \quad (10)$$

where D_L is the diffusivity of hydrogen sulfide in the liquid.

$$J_{ai} = -D_a \left(\frac{dC}{dz} \right)_{(0,t_a)} \quad \text{at } z = 0 \text{ in the gas phase} \quad (11)$$

and therefore:

$$= -D_L \left(\frac{dC}{dz} \right)_{(0,t_L)} = -D_a \left(\frac{dC}{dz} \right)_{(0,t_a)} \quad (12)$$

Hydrogen sulfide flux, J , is the diffusion flux at the top of the air film, determined the flux by the following relationship at the interface of the air film and turbulent region:

$$J_a = -D_a \left(\frac{dC}{dz} \right) \text{ at } z = t_a \quad (13)$$

Using equation (9) with $z = t_a$:

$$J_a = -D_a r_a \left(\frac{C_a (e^{r_a t_a} + e^{-r_a t_a}) - C_{ai} (e^{(t_a - t_a)r_a} + e^{-(t_a - t_a)r_a})}{e^{r_a t_a} - e^{-r_a t_a}} \right) \quad (14)$$

$$J_a = -D_a r_a \left(\frac{C_a (e^{r_a t_a} + e^{-r_a t_a}) - C_{ai} (1 + 1)}{e^{r_a t_a} - e^{-r_a t_a}} \right)$$

The concentration at the gas and liquid interface, C_{ai} and C_{Li} , respectively, are related by the Henry's Law constant, H , (temperature dependent equation given in Section 4.5.3) through the following relation:

$$C_{ai} = H C_{Li} \quad (15)$$

and therefore,

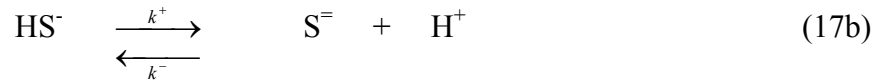
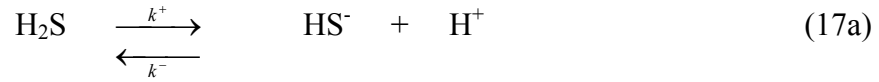
$$J_a = -D_a r_a \left(\frac{C_a (e^{r_a t_a} + e^{-r_a t_a}) - 2H C_{Li}}{e^{r_a t_a} - e^{-r_a t_a}} \right) \quad (16)$$

We now need to determine C_{Li} , which is determined by the chemical and mass transfer properties in the liquid film. This is discussed in the following section for two different liquid phase conditions.

4.3.3 Mass Transfer in the Liquid Film

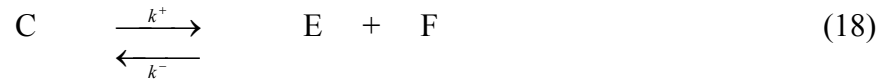
4.3.3.1 MTCR (I): pH Constant Throughout Liquid Film

In aqueous phase, molecular hydrogen sulfide is in equilibrium with the bisulfide ion and hydrogen ion as shown:



Since the equilibrium reaction of HS^- with $\text{S}^{=}$ occurs only above pH of 12, well above the practical range of an anaerobic swine lagoon, only the reaction of equilibrium reaction of H_2S with HS^- is considered. For this modeling exercise, pH is assumed constant.

Equation 17a may be generically rewritten as:

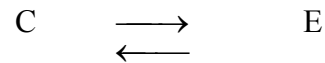


At steady state: $k^+[\text{C}] = k^-[\text{E}][\text{F}]$

$$\text{Therefore:} \quad K_L = \frac{k^+}{k^-} = \frac{[\text{E}][\text{F}]}{[\text{C}]} \quad (19)$$

Where K_L (same as $K_{a,1}$) is the rate dissociation constant for H_2S (mole L^{-1})

Using an equation of the form:



$$\text{At steady state:} \quad K_L^* = \frac{[\text{E}]}{[\text{C}]} = \frac{[\text{E}][\text{F}]}{[\text{C}][\text{F}]} = \frac{[K_L]}{[\text{F}]} \quad (20)$$

Using single reactant and single product, the flux of the total C component within the reacting liquid film phase is given by the following relationship (Olander, 1960):

$$J_{L1} = \left(\frac{D_C}{t_L} \right) (C_L - C_{Li}) \left(1 + \frac{D_E}{D_C} K_L^* \right)$$

$$J_{L1} = \left(\frac{D_C}{t_L} \right) (C_L - C_{Li}) \left(1 + \frac{D_E}{D_C} \frac{K_L}{F} \right)$$

The hydrogen sulfide flux at the liquid interface can therefore be calculated by:

$$J_{L1} = \left(\frac{D_{H_2S}}{t_L} \right) (C_L - C_{Li}) \left(1 + \frac{D_{HS^-}}{D_{H_2S}} \frac{K_L}{[H^+]} \right) \quad (21)$$

where D_{H_2S} and D_{HS^-} are the diffusion coefficients for H_2S and HS^- and t_L is the liquid film thickness.

From equation (12), at the air-liquid interface, the fluxes are equal, and so:

$$J_{L1} = \left(\frac{D_{H_2S}}{t_L} \right) (C_L - C_{Li}) \left(1 + \frac{D_{HS^-}}{D_{H_2S}} \frac{K_L}{[H^+]} \right) = -D_a \left(\frac{dC}{dz} \right)_{(t_a, 0)} \quad \text{at } z = 0$$

The concentration in the air phase is determined by equation (10) and therefore:

$$J = \left(\frac{D_{H_2S}}{t_L} \right) (C_L - C_{Li}) \left(1 + \frac{D_{HS^-}}{D_{H_2S}} \frac{K_L}{[H^+]} \right) = -D_a r_a \left(\frac{C_a (e^{r_a \times 0} + e^{-r_a \times 0}) - C_{ai} (e^{(0-t_a)r_a} + e^{-(0-t_a)r_a})}{e^{r_a t_a} - e^{-r_a t_a}} \right)$$

Simplifying the above equation and considering equation (15), $C_{ai} = HC_{Li}$, Malik (1999)

further derived the following relationship between C_{Li} , C_L , and C_a :

$$C_{Li} = \frac{\frac{2D_a C_a r_a}{e^{r_a t_a} - e^{-r_a t_a}} + C_L \frac{D_{H_2S}}{t_L} \left(1 + \frac{D_{HS^-}}{D_{H_2S}} \frac{K_L}{[H^+]} \right)}{HD_a r_a \left(\frac{e^{r_a t_a} + e^{-r_a t_a}}{e^{r_a t_a} - e^{-r_a t_a}} \right) + \frac{D_{H_2S}}{t_L} \left(1 + \frac{D_{HS^-}}{D_{H_2S}} \frac{K_L}{[H^+]} \right)} \quad (22)$$

Equation (22) gives the value of C_{Li} , which is then substituted into equation (16) to calculate the hydrogen sulfide flux values.

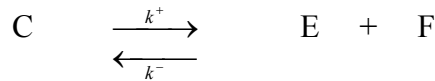
4.3.3.2 Mass Transport with Chemical Reactions (II): pH Gradient In Liquid Film

For the liquid phase, since the reaction of hydrogen sulfide is reversible, the overall reaction rate will depend on the direction of the reaction. Olander (1960) has provided equations to predict the effect of various types of infinitely rapid equilibrium chemical reactions on the liquid-phase mass transfer coefficient; however, none of these reactions consider 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-reaction single-product, this model considers the entire equilibrium reaction, with 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^+).

As discussed in the previous section, hydrogen sulfide dissociates to produce the bisulfide anion and hydrogen ion as per equation (16):



For this modeling exercise, pH is not assumed to be constant. We recall equation (17):



And equation (18)

$$K_L = \frac{k^+}{k^-} = \frac{EF}{C} \text{ for all } z$$

Where:

$$K_L = \text{Rate dissociation constant for } \text{H}_2\text{S} \text{ (mole L}^{-1}\text{)}$$

The material balances are given as follows:

$$D_C \frac{d^2 C}{dz^2} + D_E \frac{d^2 E}{dz^2} = 0 \quad (23)$$

$$D_C \frac{d^2 C}{dz^2} + D_F \frac{d^2 F}{dz^2} = 0 \quad (24)$$

$$D_E \frac{d^2 E}{dz^2} - D_F \frac{d^2 F}{dz^2} = 0 \quad (25)$$

Equations (23) and (24) are dependent equations and therefore either equation may be used. Selecting equation (23), the general solution is given by:

$$D_C C + D_E E = \alpha_1 z + \alpha_2 \quad (26)$$

Where α_1 and α_2 are constants in the equation.

Equation (25) is an independent equation and the general solution is given by:

$$D_E E - D_F F = \beta_1 z + \beta_2 \quad (27)$$

Where β_1 and β_2 are constants in the equation.

For this scenario, the boundary conditions are as follows:

$$\text{At } z = t_L, \quad C_L(t_L) = C_{Li} \quad (28)$$

$$E_L(t_L) = E_{Li} \quad (29)$$

$$F_L(t_L) = F_{Li} \quad (30)$$

$$\text{At } z = 0, \quad C_L(0) = C_L \quad (31)$$

$$E_L(0) = E_L \quad (32)$$

$$F_L(0) = F_L \quad (33)$$

Where C_{Li} = Concentration of C (H_2S) at the top of the liquid film (i.e., gas-liquid interface)

E_{Li} = Concentration of E (HS^-) at the top of the liquid film

F_{Li} = Concentration of F (H^+) at the top of the liquid film

C_L = Concentration of C (H_2S) in the bulk liquid phase

E_L = Concentration of E (HS^-) in the bulk liquid phase

$$F_L = \text{Concentration of } F (H^+) \text{ in the bulk liquid phase}$$

The final boundary conditions reflect the inability of E and F to penetrate the gas-liquid interface ($z = t_L$):

$$D_E \frac{dE}{dz} = 0 \quad (34)$$

$$D_F \frac{dF}{dz} = 0 \quad (35)$$

Applying the boundary condition in equations (28) and (29) to the general equation (26), we obtain:

$$D_C C_{Li} + D_E E_{Li} = \alpha_1 t_L + \alpha_2 \quad (36)$$

And by applying (31) and (32) to (26):

$$D_C C_L + D_E E_L = \alpha_2 \quad (37)$$

Substituting (37) into (36):

$$D_C C_{Li} + D_E E_{Li} = \alpha_1 t_L + D_C C_L + D_E E_L \quad (38)$$

Taking the derivative with respect to z of both sides of equation (26) and applying boundary condition (34)

$$J_{L2} = -D_C \frac{dC}{dz} = -\alpha_1$$

(39)

Where J is the H_2S flux at the liquid-air interface.

Substituting (39) into (38):

$$D_C C_{Li} + D_E E_{Li} = -J t_L + D_C C_L + D_E E_L,$$

$$\text{Or} \quad J_{L2} = \frac{1}{t_L} (D_C C_L - D_C C_{Li} + D_E E_L - D_E E_{Li}) \quad (40)$$

Applying the boundary condition in equations (28) and (29) to the general equation (26), we obtain:

$$D_E E_{Li} - D_F F_{Li} = \beta_1 t_L + \beta_2 \quad (41)$$

Taking the first derivative with respect to z of both sides of equation (27) and applying boundary conditions, (33) and (34), at $z = t_L$ we find that β_1 is zero and thus,

$$D_E E - D_F F = \beta_2 \text{ for } 0 \leq z \leq t_L \quad (42)$$

At the boundaries,

$$D_E E_L - D_F F_L = \beta_2 \text{ and} \quad (43)$$

$$D_E E_{Li} - D_F F_{Li} = \beta_2 \quad (44)$$

In order to determine the concentration of C_{Li} , the gas-phase flux equation is set equal to the liquid-phase flux equation (40). However, the concentration of E_{Li} (HS^- at the top of the liquid film) is also unknown and must be solved for in terms of C_{Li} . In order to do this, we make use of equation (44). By multiplying both sides of equation (44) by E_{Li} we obtain:

$$D_E E_{Li}^2 - D_F E_{Li} F_{Li} = \beta_2 E_{Li} \quad (45)$$

From (19) it can be seen that $K_L C = EF$ (i.e., $K_L C_{Li} = E_{Li} F_{Li}$) and therefore:

$$D_E E_{Li}^2 - D_F K_L C_{Li} = \beta_2 E_{Li}$$

Or
$$D_E E_{Li}^2 - \beta_2 E_{Li} - D_F K_L C_{Li} = 0 \quad (46)$$

Applying the quadratic equation to solve for E_{Li} :

$$E_{Li} = \frac{-(-\beta_2) \pm \sqrt{\beta_2^2 + 4D_E D_F K_L C_{Li}}}{2D_E}$$

Or
$$E_{Li} = \frac{\beta_2 + \sqrt{\beta_2^2 + 4D_E D_F K_L C_{Li}}}{2D_E} \quad (47)$$

since the concentration must be a positive value.

Substituting equation (47) into (40) we have:

$$\begin{aligned} J_{L2} &= \frac{1}{t_L} \left[D_C C_L - D_C C_{Li} + D_E E_L - D_E \left(\frac{\beta_2}{2D_E} + \sqrt{\beta_2^2 + 4D_E D_F K_L C_{Li}} \right) \right] \\ J_{L2} &= \frac{1}{t_L} \left[D_C (C_L - C_{Li}) + D_E \left\{ E_L - \left(\frac{\beta_2}{2D_E} + \frac{\sqrt{\beta_2^2 + 4D_E D_F K_L C_{Li}}}{2D_E} \right) \right\} \right] \\ J_{L2} &= \frac{1}{2t_L} \left(2D_C C_L - 2D_C C_{Li} + 2D_E E_L - \beta_2 - \sqrt{\beta_2^2 + 4D_E D_F K_L C_{Li}} \right) \end{aligned} \quad (48)$$

Where β_2 is determined by $D_E E_L - D_F F_L$

The equation for flux in the gas-phase is given by equation (16). If $\Phi = e^{r_a t_a} + e^{-r_a t_a}$ and

$\Omega = e^{r_a t_a} - e^{-r_a t_a}$, we obtain:

$$J_a = -D_a r_a \left(\frac{C_a \Phi - 2H C_{Li}}{\Omega} \right)$$

Or
$$J_a = \frac{1}{\Omega} (-D_a r_a C_a \Phi + 2D_a r_a H C_{Li}) \quad (49)$$

We can now solve for C_{Li} by setting (48) and (49) equal to each other:

$$\begin{aligned} \frac{1}{\Omega} (-D_a r_a C_a \Phi + 2D_a r_a H C_{Li}) &= \\ \frac{1}{t_L} \left(2D_C C_L - 2D_C C_{Li} + 2D_E E_L - \beta_2 + \sqrt{\beta_2^2 - 4D_E D_F K_L C_{Li}} \right) \end{aligned} \quad (50)$$

By rearranging the equation and squaring both sides we obtain a non-linear equation.

The quadratic formula is applied to solve for C_{Li} and the equation is given by:

$$C_{Li} = \frac{\Omega \sqrt{4D_C \Theta K_L \Omega C_L D_E D_F + 4\Theta K_L t_L \Phi D_a r_a C_a D_E D_F} + K_L \Omega D_E^2 D_F (K_L \Omega D_F + 4\Theta) E_L - 2\Theta \beta_2 K_L \Omega D_E D_F + \Theta^2 \beta_2^2 + 2D_C \Theta \Omega C_L + 2\Theta t_L \Phi D_a r_a C_a + \Omega (2D_E (K_L \Omega D_F + \Theta D_E - \Theta \beta_2))}{2\Theta^2} \quad (51)$$

Where $\Theta = D_C \Omega + 2D_a r_a H t_L$

Equation (51) gives the value of C_{Li} , which is substituted into equation (16) to calculate the hydrogen sulfide flux values for the condition pH gradient in the quiescent liquid film.

4.4 Mass Transport with No Chemical Reaction (MTNCR) Model for Atmospheric Hydrogen Sulfide Emission

Hydrogen sulfide transport takes place from the bulk liquid phase through the liquid film phase to the air-liquid interface, where it further diffuses through the air film to the turbulent air phase. It is assumed that the turbulent air and liquid regions are well mixed and that the main resistance to gas transport is from the gas and liquid phase interfacial layers, where the gas transfer is by molecular processes across these regions (Liss and Slater, 1974). The concentrations of hydrogen sulfide in the turbulent gas and liquid regions are given by C_a and C_L and the concentrations at the respective interfacial layers are given by C_{ai} and C_{Li} . As given by Lewis and Whitman (1924):

Flux in the gas phase

$$J_a = -k_a(C_a - C_{ai}) \quad (52)$$

Flux in the liquid phase

$$J_L = -k_L(C_{Li} - C_L) \quad (53)$$

At the interface, as given by equation (15), $C_{ai} = H C_{Li}$.

From equations (52), (53), and (11):

$$C_{Li} = \frac{C_{ai}}{H} = \frac{k_a C_a + k_L C_L}{k_a H + k_L} \quad (54)$$

From equation (53) and (54):

$$J = -\frac{k_a k_L}{k_a H + k_L} (C_a - H C_L) \quad (55)$$

$$J = -K_{OL} (C_a - H C_L) \quad (56)$$

Where K is the overall mass transfer coefficient and can be expressed by (Whitman, 1923):

$$\frac{1}{K_{OL}} = \frac{H}{k_L} + \frac{1}{k_a} \quad (57)$$

where k_a and k_L are the gas and liquid mass transfer coefficients, respectively, and H is the Henry's Law constant. Equations and values used to obtain k_a , k_L , and H are provided in Section 4.5.3.

4.5. Basic Equations to Solve for Concentration at the Liquid Interface

4.5.1 Kinetic Viscosity Calculations

Density of Moist Air, ρ_a (g cm⁻³) Source: Arogo *et al.* (1999)

$$\rho_a = 0.001 \left(\frac{353}{T_a} \right) \left(\frac{760 - 0.3783 * RH * e^{0.0596 * T_a - 14.6135}}{760} \right) \quad (58)$$

RH = relative humidity (%)

T_a = air temperature (°K)

Density of Water, ρ_w (g cm⁻³) Source: Malik (1999)

$$\rho_w = \frac{\left(999.84 + 16.95 * T_L - 7.99 \times 10^{-3} * T_L^2 - 46.17 \times 10^{-6} * T_L^3 \right) + 105.56 \times 10^{-9} * T_L^4 - 280.54 \times 10^{-12} * T_L^5}{\left(1 + 16.88 \times 10^{-3} * T_L^5 \right)} \quad (59)$$

T_L = lagoon temperature (°C)

Dynamic Viscosity of Air, μ_a (kg m⁻¹ s⁻¹) Source: Jacobson (1999)

$$\mu_a = 1.8325 \times 10^{-5} \left(\frac{416.16}{(273.15 + T_a) + 120} \right) \left(\frac{273.15 + T_a}{296.16} \right)^{3/2} \quad (60)$$

T_a = air temperature (°C)

Dynamic Viscosity of Water, μ_w (cP= 10⁻² g cm⁻¹ s⁻¹) Source: Malik (1999)

For $0 < T_L < 20$:

$$\log_{10} \left(\frac{\mu_w}{100} \right) = \frac{1301}{998.333 + 8.1855 * (T_L - 20) + 0.00585 * (T_L - 20)^2} - 3.30233 \quad (61)$$

For $20 < T_L < 100$:

$$\log_{10} = \frac{1.3272 * (20 - T_L) - 0.0011 * (T_L - 20)^2}{T_L + 105} \quad (62)$$

T_L = lagoon temperature (°C)

Once the density and dynamic viscosity of air and water have been determined, the kinetic viscosity can then be calculated. The equations are of the following form:

Kinetic Viscosity of Air, ν_a (cm² s⁻¹)

$$\nu_a = \frac{\mu_a}{\rho_a} \quad (63)$$

Kinetic Viscosity of Water, ν_w (cm² s⁻¹)

$$\nu_w = \frac{\mu_w}{\rho_w} \quad (64)$$

4.5.2 Diffusivity Calculations

Diffusivity of Gases in Water, D_w (cm² s⁻¹)

Based on Wilke-Chang correlation (Cussler, 1997):

$$D_w = \frac{7.4 \times 10^{-8} (273 + T_L)(\phi MW)^{1/2}}{\mu_w * V_1} \quad (65)$$

ϕ = solute-solvent interaction factor (2.26 for water)

MW = molecular weight of water (g mol^{-1})

V = molar volume of gaseous specie at boiling point (cm^3)

Cussler (1997) reports a value of $1.41 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $9.31 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for the diffusion coefficients of molecular hydrogen sulfide and hydrogen ion, respectively, in an infinite dilution of water at 25°C . Dinius and Redding (1972) calculated an average value of $5.29 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for the diffusion coefficient of bisulfide at various ionic strengths and 25°C . Since T_L and μ_w are the only parameters that may vary, the above equation allows for the following correlation at different temperatures related to $D_{w,25}$ (Malik, 1999):

$$D_{w,T} = D_{w,25} \left(\frac{273 + T / \mu_T}{298 / \mu_{25}} \right) \quad (66)$$

μ_T = dynamic viscosity of water at temperature, T

μ_{25} = dynamic viscosity of water at 25°C ($0.00887 \text{ g cm}^{-1} \text{ s}^{-1}$)

Diffusivity of Hydrogen Sulfide in Air, D_a ($\text{cm}^2 \text{ s}^{-1}$)

The diffusivity of any gaseous substance in air may be calculated using Fuller, Schettler, and Giddings (1966) empirical relations (from Cussler, 1997):

$$D_a = 10^{-3} \frac{(273 + T_a)^{1.75} \left(\frac{1}{MW_1} + \frac{1}{MW_2} \right)^{1/2}}{p \left[\left(\sum_i V_{i1} \right)^{1/3} + \left(\sum_i V_{i2} \right)^{1/3} \right]^2} \quad (67)$$

MW_1 = molecular weight of hydrogen sulfide (34 g mol⁻¹)

MW_2 = molecular weight of air (29 g mol⁻¹)

V_{i1} = diffusion volume of hydrogen sulfide (20.96 at 1 atm)

V_{i2} = diffusion volume of air (20.1 at 1 atm)

p = atmospheric pressure (1 atm)

4.5.3 Mass Transfer Coefficient Calculations

The mass transfer coefficients for air and water are calculated in order to determine the gas and liquid film thickness, respectively, and are a function of wind speed at a reference height of 10 meters (with the exception of the liquid mass transfer coefficient at low wind velocities), kinetic viscosity, and diffusivity of a gas at a given temperature. The following empirical equations (determined through laboratory wind tunnel experiments), based on specific conditions as recommended and discussed by the U.S. EPA (1994) for waste impoundments, were used:

Air Mass Transfer Coefficient, k_a (cm s⁻¹)

$$k_a = 1 \times 10^{-3} + 46.2 \times 10^{-3} * U_* * S_{ca}^{-0.67} \quad (68)$$

(Source: Mackay and Yeun, 1983)

where U_* and S_{ca} are defined as:

Friction Velocity, U_ (m s⁻¹)* (Source: Mackay and Yeun, 1983)

$$U_* = 0.01 U_{10} (6.1 + 0.63 U_{10})^{1/2} \quad (69)$$

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

Schmidt Number in Air, S_{ca} , dimensionless

$$S_{ca} = \frac{\nu_a}{D_a} \quad (70)$$

ν_a = Kinetic Viscosity of Water ($\text{cm}^2 \text{s}^{-1}$)

D_a = Diffusivity of Hydrogen Sulfide in Water, ($\text{cm}^2 \text{s}^{-1}$)

Liquid Mass Transfer Coefficient, k_L (cm s^{-1}) (at any fetch-to-depth ratio)

For $0 < U_* < 0.093$ ($0 < U_{10} < 3.25$) (Source: Springer et al., 1984),

$$k_L = 2.78 \times 10^{-6} \left| \frac{D_w}{D_{ether}} \right|^{2/3} \quad (71)$$

where D_w and D_{ether} are the diffusion coefficients for H_2S and ethyl ether in water, respectively. At low wind speeds, Springer's model implies that k_L is constant for wind speeds (U_{10}) of 0 to 3.25 m s^{-1} . Although Springer examined only the mass transfer of ethyl ether, the results are extrapolated to other solutes by the above equation (E.S. EPA, 1994).

For $0.093 < U_* < 0.3$ (Source: Mackay and Yeun, 1983)

$$k_L = 1 \times 10^{-6} + 144 \times 10^{-4} * U_*^{2.2} * S_{cw}^{-1/2} \quad (72)$$

For $U_* > 0.3$ (Source: Mackay and Yeun, 1983)

$$k_L = 1 \times 10^{-6} + 34.1 \times 10^{-4} * U_* * S_{cw}^{-1/2} \quad (73)$$

Schmidt Number in Water, S_{cw} , dimensionless

$$S_{cw} = \frac{\nu_w}{D_w} \quad (74)$$

$$\nu_w = \text{Kinetic Viscosity of Water (cm}^2 \text{ s}^{-1}\text{)}$$

$$D_w = \text{Diffusivity of Hydrogen Sulfide in Water, (cm}^2 \text{ s}^{-1}\text{)}$$

The Mackay and Yeun equations were obtained by examining the transport of 11 different solutes with varying Henry's Law constant values. The Schmidt numbers for these compounds are within a factor of two compared to the calculated value for H₂S in this study. The Henry's Law constant for hydrogen sulfide (discussed below) is within the range given for these 11 compounds, on the order of 10⁻³ atm m³ mol⁻¹. It should be noted that Mackay and Yeun (1983) conducted their wind tunnel experiments at wind velocities ranging from ~6-13 m s⁻¹. Hence, the Springer equation was applied at low wind velocities for this modeling exercise. This equation is reported to be applicable for all fetch-to-depth ratios (U.S. EPA, 1994).

It is reasonable to assume that the liquid mass transfer coefficient for liquid hog waste may be lower than water, due to possible variations in viscosity and diffusion processes. Yongsiri et al. (2005) observed a 40% reduction for the liquid mass transfer coefficient of hydrogen sulfide in sewage networks compared to de-ionized water. Based on the results of this study, a correction factor of 0.6 was applied to the liquid mass transfer coefficient equations for model calculations to predict emissions from liquid hog waste. Therefore equations (71), (72), and (73) may be calculated as:

$$k_L' = 0.6 * k_L \quad (75)$$

The respective film thicknesses may then be determined by the following relations:

Air Film Thickness, t_a (cm)

$$t_a = \frac{D_a}{k_a} \quad (76)$$

D_a = diffusivity of H₂S in air

k_a = air mass transfer coefficient

Liquid Film Thickness, t_L (cm)

$$t_L = \frac{D_L}{k_L} \quad (77)$$

D_L = diffusivity of H₂S in water

k_L = liquid mass transfer coefficient

Henry's Law Constant, H (mol L⁻¹_(g) / mol L⁻¹_(l))

Metcalf and Eddy (1979) report values for Henry's Law constant of hydrogen sulfide as a function of temperature from 0-60°C. These values were graphed (Figure 4.3) and a third order polynomial equation was obtained in order to determine the Henry's Law constant for all temperatures between 0 and 60°C:

$$H = -4 \times 10^{-7} * T_L^3 + 4 \times 10^{-5} * T_L^2 + 0.0067 * T_L + 0.2147 \quad (78)$$

where H is the Henry's Law constant for H₂S and T_L is the liquid temperature.

Al-Haddad et al. (1989) experimentally evaluated Henry's Law constant of H₂S from 20-40°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; U.S. EPA, 1974), and it was reported that the more complex chemical composition did not appear to influence Henry's Law constant. Yongsiri et al (2005) have since corroborated this finding.

4.6 Results and Discussion

4.6.1 Parameters Affecting Hydrogen Sulfide Emissions

The three modeling approaches discussed previously in Sections 4.3 and 4.4 provide flux dependence for hydrogen sulfide emissions on lagoon temperature, lagoon

pH, and aqueous sulfide content in the lagoon as well as meteorological factors such as ambient temperature, wind speed, and the concentration of H_2S in the ambient air.

Sensitivity analyses for various parameters were performed on each model and model performance was evaluated by comparing results to measured fluxes (see Chapter 3).

Gas phase H_2S concentrations were measured during the same period as the lagoon flux measurements. Model parameters and results are discussed in the following sections.

4.6.2 Mass Transport with No Chemical Reactions (MTNCR): Model Parameter Considerations

Hydrogen sulfide flux is calculated from equation (56). The overall mass transfer coefficient is determined by both gas and liquid mass transfer coefficients (equations 68, 71- 73) and Henry's law constant (equation 78). Temperature dependence on the Henry's Law constant as well as diffusivity, viscosity, and rate dissociation constant has been taken into account. The effect of pH on the H_2S fraction of total sulfide in aqueous solution is considered by Equation (1). Wind speed variation is considered through the determination of mass transfer coefficients. Calculations were made for a range of values for aqueous sulfide concentration, pH, lagoon and air temperature, wind speed, and ambient H_2S concentration. Table 4.1 provides sensitivity analysis results for hydrogen sulfide flux using this equilibrium approach.

4.6.3 Mass Transport with Chemical Reactions (MTCR) Model (I): Model Parameter Considerations

Hydrogen sulfide fluxes are determined from equations (16) and (21). In the gas phase, only forward reactions with the hydroxyl radical (OH) were considered in order to calculate the overall reaction rate constant, k_{ra} as given by equation (6). In the liquid

phase the reversible reaction of hydrogen sulfide was considered and flux transport through the liquid film was calculated by Equation (21), given by Olander (1960). In this model, the pH is assumed to be constant throughout the liquid film.

Film thickness is defined by the diffusivity of hydrogen sulfide divided by the mass transfer coefficient for the respective layer (gas or liquid). The mass transfer coefficient equations were the same as those used for the MTNCR Model.

Calculations were made for a range of values for aqueous sulfide concentration, pH, lagoon and air temperatures, wind speed, and ambient H₂S concentration. Table 4.2 provides sensitivity analysis results for hydrogen sulfide flux using this mass transfer with chemical reactions model (MTCR) approach. Additionally, the model was tested and it was determined that, considering negligible chemical reaction in the gas and liquid phases, the results of this MTCR Model I were similar to the MTNCR Model.

4.6.4 Mass Transport with Chemical Reactions (MTCR) Model (II): Model Parameter Considerations

For this MTCR Model, hydrogen sulfide fluxes are determined from equations (16) and (48). The gas phase is treated the same as for the MTCR Model I. In the liquid phase the reversible reaction of hydrogen sulfide was considered and flux transport through the liquid film was calculated in Section 4.3.3.2. For this model, it was considered that a pH gradient may exist in the liquid film. The film thickness for each layer was calculated using the same equations for the MTCR I Model. Calculations were made for the same variables and ranges of values used in MTCR Model I. Table 4.2 provides sensitivity analysis results for hydrogen sulfide flux using this MTCR Model II approach.

4.6.5 Sensitivity Analysis

Practical ranges of aqueous sulfide content, lagoon pH, lagoon temperature, air temperature, wind speed, and ambient H₂S concentration have been considered for the sensitivity analysis. The effect of each parameter was examined by varying the values of the parameter throughout the respective range while holding every other parameter value constant. The constant values were chosen based on annual average values that were measured at an experimental swine lagoon site in eastern North Carolina, although the aqueous sulfide content used in the sensitivity analysis is slightly lower than the annual average (see Chapter 3). It is noted that the measured pH range was much smaller (7.9-8.2) but the values used in the sensitivity analysis might be typical at other swine lagoons. The parameters have been assigned the following ranges and constant values:

Parameter	Range	Constant Value
Aqueous sulfide content (mg L ⁻¹)	0 – 30	2.0
Lagoon pH	6.5 – 8.5	8.1
Lagoon temperature (°C)	0 - 35	19
Air temperature (°C)	0 - 35	16
Wind speed at 10m height (m s ⁻¹)	0 – 8	1.3
Ambient H ₂ S concentration (µg m ⁻³)	0 – 50	10.0

4.6.5.1 Effect of Aqueous Sulfide Concentration

Aqueous sulfide concentration was varied from 0 to 30 mg L⁻¹ (Figure 4.4). A linear increase was observed for all three models. Predicted emissions for the MTCR Model I and MTCR Model II were ~6.0 and 6.2 times higher, respectively, than the MTNCR Model based on the increase in aqueous sulfide. As sulfide concentration was increased the rate of predicted emissions for The MTCR Model II was ~4% higher than MTCR Model I. In diluted water H⁺ diffuses more than 6 times faster than H₂S.

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 and accounting for the higher flux predicted in MTCR Model II.

4.6.5.2 Effect of Lagoon pH

Lagoon pH controls the chemical equilibrium of H_2S - HS^- - $\text{S}^{=}$ system in the aqueous phase. The pH was varied in each model from 6.5 to 8.5 (Figure 4.5). Model results show that the MTNCR Model has a higher increase in flux as the pH is decreased. However, due to other parameters, the predicted flux is lower than the flux predicted by both MTCR Models at all pH ranges. The MTCR Model II shows a slightly lower flux increase rate as pH is decreased compared to the MTCR Model I.

4.6.5.3 Effect of Lagoon temperature

Lagoon temperature was varied from 0°C to 35°C (Figure 4.6). For each model, flux decreased as lagoon temperature increased. Since diffusivity and viscosity generally increase as temperature increases, this finding may appear to be counterintuitive. However, considering equation (1), the fraction of hydrogen sulfide present in the liquid is a function of the H_2S acidity constant, $K_{a,1}$ (same as K_L). As $K_{a,1}$ increases the H_2S dissociation increases (U.S. EPA, 1974; Yongsiri et al., 2004) and therefore less molecular H_2S is available for transfer across the gas-liquid interface. Figure 4.7 shows the percent decrease at pH = 7.0 (a) and pH = 8.0 (b) calculated from equation (1). The fraction of undissociated H_2S decreases by almost 30% at a pH value of 7.0 while the decrease is smaller (~10%) at a higher pH value of 8.0. For the range of temperatures used in this analysis, the MTCR I and II Models show a decrease in emissions of 13%

and 10%, respectively, and the MTNCR Model predicts a decrease in flux of ~61% at pH equal to 8.1.

4.6.5.4 Effect of Air Temperature

Air temperature was varied from 0°C to 35°C (Figure 4.10). For all three models, change in H₂S flux was negligible as air temperature increased.

4.6.5.5 Effect of Wind Speed

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). The gas mass transfer coefficient, which is a function of wind speed, therefore is expected to have little effect on the hydrogen sulfide emissions process. Wind speed was varied from 0 to 8 m s⁻¹ (Figure 4.9). The U.S. EPA (1994) has recommended several equations to calculate the liquid mass transfer coefficient based on various fetch-to-depth ratios and wind velocities. For liquid mass transfer coefficient, at friction velocities <0.093 m s⁻¹ the Springer correlation may be applied. Therefore, wind speed is not considered to determine liquid mass transfer. At friction velocities > 0.093 m s⁻¹, Mackay and Yeun formulations, which rely on wind speed as well as the Schmidt number, are used. During the sensitivity analysis, as the wind speed was increased above 3.25 m s⁻¹, H₂S flux increased exponentially. Wind speed variation from 3.0 – 8.0 m s⁻¹ predicts a flux change from 19 µg m⁻² min⁻¹ to 99 µg m⁻² min⁻¹ for the MTNCR Model, and more dramatic changes for the MTCR I Model, 165 µg m⁻² min⁻¹ to 836 µg m⁻² min⁻¹ and the MTCR II Model, from 171 µg m⁻² min⁻¹ to 884 µg m⁻² min⁻¹.

4.6.5.6 Effect of Ambient H₂S Concentration

Ambient H₂S concentration was varied from 0-50 $\mu\text{g m}^{-3}$ (Figure 4.10). For all three models, change in H₂S flux was negligible as ambient concentration increased.

4.6.5.7 Effect of Film Thickness

Sensitivity analysis results for the above parameters result in film thicknesses ranging from 0.007-0.086 cm for liquid film and 0.117-1.708 cm for gas film. The effect of gas and liquid film thicknesses were examined under various temperatures and pH values 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. Sensitivity analysis results are presented in Table 4.3. Lower film thicknesses are generally associated with more turbulent conditions outside the film (Quinn and Otto, 1971; Liss and Slater, 1974). As the liquid film thickness was increased, emissions for both models decreased almost linearly. There was negligible change in emissions as the gas film thickness was changed. With the assumptions used in the model, results imply that hydrogen sulfide flux is driven primarily by the liquid phase, as reported by Lewis and Whitman (1924) and Liss and Slater (1974). Hence, the contribution of environmental parameters on the air side (i.e., air temperature and low 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 (which increases as liquid temperature increases). However, as noted in Section 4.5.5.5, wind speeds above 3.25 m s^{-1} are expected to affect the flux (exponential increase) as the surface stress increases.

4.6.6 Model Results Compared with Experimental Data

Measurements of H₂S flux as well as lagoon and meteorological parameters were made at a commercial swine facility in 2004-2005 (see Chapter 3). Data from the fall, spring and summer experimental periods (winter was not included because emissions were generally negligible) was analyzed using SAS statistical software (SAS Institute, Cary, NC) to perform multiple linear regression analysis. Hourly averaged measured flux values, lagoon temperature, and pH, as well as seasonally averaged aqueous sulfide concentration, were used to determine the experimental model equation. Air temperature and wind speed were not included because they are expected to have little impact on the emission process (for wind velocities < 3.25 m s⁻¹). Flux measurements made at higher wind velocities were not considered in this analysis (< 8 % of the data set). The equation obtained by multiple linear regression analysis is given by:

$$\text{H}_2\text{S Flux} = 234.137 + 0.405 \cdot C_{\text{TS}} - 0.117 \cdot T_{\text{L}} - 28.655 \cdot \text{pH} \quad (79)$$

where H₂S flux is expressed in units of $\mu\text{g m}^{-2} \text{min}^{-1}$ and C_{TS} and T_{L} are total sulfide concentration in mg L^{-1} and lagoon temperature in °C, respectively, and $R^2 = 0.67$, p -value < .0001, $n = 314$. It is noted that the pH only varied from ~7.9-8.2 during the three experimental periods.

Figure 4.11 presents a comparison of the relationship between plots of predicted H₂S flux versus lagoon temperatures for the three models and the predicted flux based on statistical analysis from the experimental data. Aqueous sulfide concentration, air temperature, wind speed, and ambient H₂S concentration were held constant at 2 mg L^{-1} , 16°C, 1.3 m s^{-1} , and 10 $\mu\text{g m}^{-3}$, respectively, for all comparisons. Additionally fluxes measured when sulfide concentration was $2 \pm 1 \text{ mg L}^{-1}$, air temperature was $16 \pm 5 \text{ }^\circ\text{C}$,

pH 8.0 ± 0.1 , wind velocity $\leq 3.25 \text{ m s}^{-1}$, and were plotted to compare with the mass transfer models.

At the coolest temperature, 5°C , both MTCR Models predicted emissions more than 3.6 and 25 times higher than the MTNCR and linear regression model, respectively. The MTNCR model predicted emission ~ 7 times higher than the linear regression model. As temperatures were increased to 35°C the MTNCR and Linear Regression Models predicted a decrease in emissions of 54 and 68%, respectively, while both MTCR Models predicted much lower flux decreases of $\sim 9\%$. Therefore, at a higher lagoon temperature of 35°C , the difference in estimated fluxes between the models was even more dramatic. The MTCR Models predicted flux more than 7 and 70 times higher than MTNCR and linear regression models, respectively, and the MTCR Model estimated flux to be ~ 10 times higher than the linear regression model. Although the flux estimations vary greatly between models, there is agreement for all models, including linear regression, indicating a decrease in emissions as lagoon temperatures are increased. The measured values plotted were more than 25 and 100 times lower than the MTNCR and both MTCR Models, respectively.

In order to examine the diurnal variations of the emission rates predicted emissions were compared to flux values measured during the summer experimental period. Figure 4.12 provides hourly averaged H_2S flux from June 14-18, 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 June 17, 2005, along with measured lagoon and environmental parameters are provided in Table 4.4.

Table 4.5 shows the average measured H₂S 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 H₂S 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 H₂S and HS⁻, the rate reaction constant for H₂S with the hydroxyl radical in the atmosphere, and the H₂S rate dissociation constant. Uncertainties with these parameters are discussed in further detail in the following section.

4.6.7 Modeling Uncertainties

As shown in the previous section, each model showed good qualitative agreement in diurnal variation but predicted a significantly higher H₂S 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 diffusivities, rate 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.

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 Dinius and Redding (1972), who conducted laboratory experiments to determine the diffusivities of H_2S , HS^- , and S^{2-} . The reported values for H_2S were ~ 2 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 incorrect 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 2, 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. Arogo et al. (2003) conducted a laboratory experiment for dissociation constant of ammonium ion in deionized water and anaerobic 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 H_2S in similar conditions. Additionally, as discussed in Section 4.5.3, 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 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. This lack of information may also significantly affect predicted emission rates.

Predicted modeled emissions were 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 to 1.5 mg L^{-1} , 0.1 to 9.4 mg L^{-1} , and 4.0 to 13.0 mg L^{-1} , during the fall, winter, and summer experimental periods. Also, samples

were only collected during daytime hours and so it is unknown if (and how much) the concentration may change over the 24-hour diurnal period. 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.

4.7 Conclusions

A process-based model 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 to the bisulfide ion. Ambient air temperature does not appear to affect emission rates. Wind velocities $< 3.25 \text{ m s}^{-1}$ at 10 m 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 more than 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 qualitative 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 was the closest, 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, sulfide concentrations, and wind speeds), be used to test and evaluate model performance in the future.

4.8 References

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Table 4.1. Results and sensitivity analysis calculations for MTNCR model.

Sulfide _{aq}	Lagoon Temp	pH	Wind Speed	Air Temp	Ambient H ₂ S Conc	H ₂ S _{aq} Conc	Schmidt Number		U _s	H	k _a	k _L	K _{oL}	H ₂ S Flux
mg L ⁻¹	°C		m s ⁻¹	°C	µg m ⁻³	mg L ⁻¹	air	water	m s ⁻¹	mol L ⁻¹ _{air} /mol L ⁻¹ _{liq}	cm s ⁻¹	cm s ⁻¹	cm s ⁻¹	µg m ⁻² min ⁻¹
0	19	8.1	1.3	16	10	0.00	0.86	1724.50	0.03	0.215	0.27	2.34E-04	2.33E-04	0.00
2	19	8.1	1.3	16	10	0.14	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	19.40
4	19	8.1	1.3	16	10	0.28	0.86	1724.50	0.03	0.242	0.27	2.34E-04	9.63E-04	38.81
6	19	8.1	1.3	16	10	0.42	0.86	1724.50	0.03	0.256	0.27	2.34E-04	9.10E-04	58.23
8	19	8.1	1.3	16	10	0.55	0.86	1724.50	0.03	0.271	0.27	2.34E-04	8.62E-04	77.65
10	19	8.1	1.3	16	10	0.69	0.86	1724.50	0.03	0.285	0.27	2.34E-04	8.18E-04	97.08
12	19	8.1	1.3	16	10	0.83	0.86	1724.50	0.03	0.300	0.27	2.34E-04	7.77E-04	116.52
14	19	8.1	1.3	16	10	0.97	0.86	1724.50	0.03	0.315	0.27	2.34E-04	7.40E-04	135.95
16	19	8.1	1.3	16	10	1.11	0.86	1724.50	0.03	0.331	0.27	2.34E-04	7.06E-04	155.40
18	19	8.1	1.3	16	10	1.25	0.86	1724.50	0.03	0.346	0.27	2.34E-04	6.75E-04	174.84
20	19	8.1	1.3	16	10	1.39	0.86	1724.50	0.03	0.362	0.27	2.34E-04	6.46E-04	194.29
22	19	8.1	1.3	16	10	1.53	0.86	1724.50	0.03	0.377	0.27	2.34E-04	6.19E-04	213.74
24	19	8.1	1.3	16	10	1.66	0.86	1724.50	0.03	0.393	0.27	2.34E-04	5.94E-04	233.19
26	19	8.1	1.3	16	10	1.80	0.86	1724.50	0.03	0.409	0.27	2.34E-04	5.71E-04	252.65
28	19	8.1	1.3	16	10	1.94	0.86	1724.50	0.03	0.425	0.27	2.34E-04	5.50E-04	272.10
30	19	8.1	1.3	16	10	2.08	0.86	1724.50	0.03	0.441	0.27	2.34E-04	5.30E-04	291.56
2	0	8.1	1.3	16	10	0.24	0.86	5574.79	0.03	0.228	0.27	2.34E-04	1.02E-03	33.14
2	5	8.1	1.3	16	10	0.20	0.86	3952.04	0.03	0.228	0.27	2.34E-04	1.02E-03	28.67
2	10	8.1	1.3	16	10	0.18	0.86	2878.29	0.03	0.228	0.27	2.34E-04	1.02E-03	24.87
2	15	8.1	1.3	16	10	0.15	0.86	2146.94	0.03	0.228	0.27	2.34E-04	1.02E-03	21.63
2	20	8.1	1.3	16	10	0.14	0.86	1622.99	0.03	0.228	0.27	2.34E-04	1.02E-03	18.88
2	25	8.1	1.3	16	10	0.12	0.86	1261.77	0.03	0.228	0.27	2.34E-04	1.02E-03	16.53
2	30	8.1	1.3	16	10	0.10	0.86	996.97	0.03	0.228	0.27	2.34E-04	1.02E-03	14.52
2	35	8.1	1.3	16	10	0.09	0.86	799.24	0.03	0.228	0.27	2.34E-04	1.02E-03	12.80
2	40	8.1	1.3	16	10	0.08	0.86	649.13	0.03	0.228	0.27	2.34E-04	1.02E-03	11.32
2	19	6.5	1.3	16	10	1.50	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	209.23
2	19	6.7	1.3	16	10	1.30	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	182.34
2	19	6.9	1.3	16	10	1.08	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	151.49
2	19	7.1	1.3	16	10	0.85	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	119.45

Table 4.1. (cont). Results and sensitivity analysis calculations for MTNCR model.

2	19	7.3	1.3	16	10	0.64	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	89.47
2	19	7.5	1.3	16	10	0.46	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	64.00
2	19	7.7	1.3	16	10	0.32	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	44.11
2	19	7.9	1.3	16	10	0.21	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	29.55
2	19	8.1	1.3	16	10	0.14	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	19.40
2	19	8.3	1.3	16	10	0.09	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	12.56
2	19	8.5	1.3	16	10	0.06	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	8.05
2	19	8.1	0	16	10	0.14	0.86	1724.50	0.00	0.228	0.10	2.34E-04	1.01E-03	19.27
2	19	8.1	1	16	10	0.14	0.86	1724.50	0.03	0.228	0.23	2.34E-04	1.02E-03	19.38
2	19	8.1	2	16	10	0.14	0.86	1724.50	0.05	0.228	0.38	2.34E-04	1.02E-03	19.42
2	19	8.1	3	16	10	0.14	0.86	1724.50	0.08	0.228	0.53	2.34E-04	1.02E-03	19.43
2	19	8.1	4	16	10	0.14	0.86	1724.50	0.12	0.228	0.70	2.47E-04	1.08E-03	20.52
2	19	8.1	5	16	10	0.14	0.86	1724.50	0.15	0.228	0.88	3.90E-04	1.71E-03	32.40
2	19	8.1	6	16	10	0.14	0.86	1724.50	0.19	0.228	1.06	5.90E-04	2.58E-03	48.98
2	19	8.1	7	16	10	0.14	0.86	1724.50	0.23	0.228	1.26	8.56E-04	3.74E-03	71.05
2	19	8.1	8	16	10	0.14	0.86	1724.50	0.27	0.228	1.46	1.20E-03	5.23E-03	99.41
2	19	8.1	1.3	0	10	0.14	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	19.40
2	19	8.1	1.3	5	10	0.14	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	19.40
2	19	8.1	1.3	10	10	0.14	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	19.40
2	19	8.1	1.3	15	10	0.14	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	19.40
2	19	8.1	1.3	20	10	0.14	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	19.40
2	19	8.1	1.3	25	10	0.14	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	19.40
2	19	8.1	1.3	30	10	0.14	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	19.40
2	19	8.1	1.3	35	10	0.14	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	19.40
2	19	8.1	1.3	40	10	0.14	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	19.40
2	20	8.1	1.3	40	0	0.14	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	19.40
2	20	8.1	1.3	40	10	0.14	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	19.40
2	20	8.1	1.3	40	20	0.14	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	19.40
2	20	8.1	1.3	40	30	0.14	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	19.40
2	20	8.1	1.3	40	40	0.14	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	19.40
2	20	8.1	1.3	40	50	0.14	0.86	1724.50	0.03	0.228	0.27	2.34E-04	1.02E-03	19.40

Table 4.2. Results and sensitivity analysis calculations for Mass Transfer with Chemical Reactions (MTCR) Models I and II.

																		MTCR I	MTCR II
Sulfide _{aq}	Lagoon Temp	pH	WS 10m	Air Temp	Ambient H ₂ S Conc	H ₂ S _{aq} Conc	H ₂ S Diff. (air)	H ₂ S Diff. (water)	HS ⁻ Diff.	Schmidt Number		U _*	H mol L ⁻¹ air/mol L ⁻¹ liq	k _a	k _L	t _L	t _a	H ₂ S Flux	H ₂ S Flux
mg L ⁻¹	°C		m s ⁻¹	°C	µg m ⁻³	mg L ⁻¹	cm ² s ⁻¹	cm ² s ⁻¹	cm ² s ⁻¹	air	water	m s ⁻¹		cm s ⁻¹	cm s ⁻¹	cm	cm	µg m ⁻² min ⁻¹	µg m ⁻² min ⁻¹
0	19	8.1	1.3	16	10	0.00	0.17	1.19E-05	4.48E-06	0.86	862	0.03	0.35	0.27	2.34E-04	0.051	0.622	0	0
2	19	8.1	1.3	16	10	0.14	0.17	1.19E-05	4.48E-06	0.86	862	0.03	0.35	0.27	2.34E-04	0.051	0.622	115	121
4	19	8.1	1.3	16	10	0.28	0.17	1.19E-05	4.48E-06	0.86	862	0.03	0.35	0.27	2.34E-04	0.051	0.622	230	241
6	19	8.1	1.3	16	10	0.42	0.17	1.19E-05	4.48E-06	0.86	862	0.03	0.35	0.27	2.34E-04	0.051	0.622	346	362
8	19	8.1	1.3	16	10	0.55	0.17	1.19E-05	4.48E-06	0.86	862	0.03	0.35	0.27	2.34E-04	0.051	0.622	462	482
10	19	8.1	1.3	16	10	0.69	0.17	1.19E-05	4.48E-06	0.86	862	0.03	0.35	0.27	2.34E-04	0.051	0.622	578	603
12	19	8.1	1.3	16	10	0.83	0.17	1.19E-05	4.48E-06	0.86	862	0.03	0.35	0.27	2.34E-04	0.051	0.622	694	724
14	19	8.1	1.3	16	10	0.97	0.17	1.19E-05	4.48E-06	0.86	862	0.03	0.35	0.27	2.34E-04	0.051	0.622	811	844
16	19	8.1	1.3	16	10	1.11	0.17	1.19E-05	4.48E-06	0.86	862	0.03	0.35	0.27	2.34E-04	0.051	0.622	927	965
18	19	8.1	1.3	16	10	1.25	0.17	1.19E-05	4.48E-06	0.86	862	0.03	0.35	0.27	2.34E-04	0.051	0.622	1044	1086
20	19	8.1	1.3	16	10	1.39	0.17	1.19E-05	4.48E-06	0.86	862	0.03	0.35	0.27	2.34E-04	0.051	0.622	1160	1206
22	19	8.1	1.3	16	10	1.53	0.17	1.19E-05	4.48E-06	0.86	862	0.03	0.35	0.27	2.34E-04	0.051	0.622	1277	1327
24	19	8.1	1.3	16	10	1.66	0.17	1.19E-05	4.48E-06	0.86	862	0.03	0.35	0.27	2.34E-04	0.051	0.622	1394	1447
26	19	8.1	1.3	16	10	1.80	0.17	1.19E-05	4.48E-06	0.86	862	0.03	0.35	0.27	2.34E-04	0.051	0.622	1511	1568
28	19	8.1	1.3	16	10	1.94	0.17	1.19E-05	4.48E-06	0.86	862	0.03	0.35	0.27	2.34E-04	0.051	0.622	1628	1689
30	19	8.1	1.3	16	10	2.08	0.17	1.19E-05	4.48E-06	0.86	862	0.03	0.35	0.27	2.34E-04	0.051	0.622	1745	1809
2	0	8.1	1.3	16	10	0.24	0.17	6.41E-06	2.41E-06	0.86	2787	0.03	0.21	0.27	2.34E-04	0.027	0.622	125	129
2	5	8.1	1.3	16	10	0.20	0.17	7.68E-06	2.89E-06	0.86	1976	0.03	0.25	0.27	2.34E-04	0.033	0.622	122	126
2	10	8.1	1.3	16	10	0.18	0.17	9.09E-06	3.42E-06	0.86	1439	0.03	0.29	0.27	2.34E-04	0.039	0.622	119	124
2	15	8.1	1.3	16	10	0.15	0.17	1.06E-05	3.99E-06	0.86	1073	0.03	0.32	0.27	2.34E-04	0.045	0.622	117	122
2	20	8.1	1.3	16	10	0.14	0.17	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.622	115	120
2	25	8.1	1.3	16	10	0.12	0.17	1.41E-05	5.30E-06	0.86	631	0.03	0.40	0.27	2.34E-04	0.060	0.622	113	119
2	30	8.1	1.3	16	10	0.10	0.17	1.60E-05	6.02E-06	0.86	498	0.03	0.44	0.27	2.34E-04	0.068	0.622	111	118
2	35	8.1	1.3	16	10	0.09	0.17	1.80E-05	6.78E-06	0.86	400	0.03	0.48	0.27	2.34E-04	0.077	0.622	110	117
2	40	8.1	1.3	16	10	0.08	0.17	2.02E-05	7.59E-06	0.86	325	0.03	0.52	0.27	2.34E-04	0.086	0.622	109	116

Table 4.2. (cont).Results and sensitivity analysis calculations for Mass Transfer with Chemical Reactions (MTCR) Models I and II.

2	20	6.5	1.3	16	10	1.50	0.17	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.622	235	236
2	20	6.7	1.3	16	10	1.30	0.17	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.622	218	219
2	20	6.9	1.3	16	10	1.08	0.17	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.622	198	200
2	20	7.1	1.3	16	10	0.85	0.17	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.622	178	181
2	20	7.3	1.3	16	10	0.64	0.17	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.622	159	162
2	20	7.5	1.3	16	10	0.46	0.17	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.622	144	147
2	20	7.7	1.3	16	10	0.32	0.17	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.622	131	135
2	20	7.9	1.3	16	10	0.21	0.17	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.622	122	126
2	20	8.1	1.3	16	10	0.14	0.17	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.622	115	120
2	20	8.3	1.3	16	10	0.09	0.17	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.622	109	116
2	20	8.5	1.3	16	10	0.06	0.17	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.622	105	114
2	20	8.1	0	16	10	0.14	0.17	1.23E-05	4.63E-06	0.86	811	0.00	0.36	0.10	2.34E-04	0.053	1.708	110	120
2	20	8.1	1	16	10	0.14	0.17	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.23	2.34E-04	0.053	0.735	114	120
2	20	8.1	2	16	10	0.14	0.17	1.23E-05	4.63E-06	0.86	811	0.05	0.36	0.38	2.34E-04	0.053	0.453	115	120
2	20	8.1	3	16	10	0.14	0.17	1.23E-05	4.63E-06	0.86	811	0.08	0.36	0.53	2.34E-04	0.053	0.321	116	120
2	20	8.1	4	16	10	0.14	0.17	1.23E-05	4.63E-06	0.86	811	0.12	0.36	0.70	3.33E-04	0.037	0.244	165	171
2	20	8.1	5	16	10	0.14	0.17	1.23E-05	4.63E-06	0.86	811	0.15	0.36	0.88	5.41E-04	0.023	0.195	267	278
2	20	8.1	6	16	10	0.14	0.17	1.23E-05	4.63E-06	0.86	811	0.19	0.36	1.06	8.33E-04	0.015	0.161	409	428
2	20	8.1	7	16	10	0.14	0.17	1.23E-05	4.63E-06	0.86	811	0.23	0.36	1.26	1.22E-03	0.010	0.136	597	628
2	20	8.1	8	16	10	0.14	0.17	1.23E-05	4.63E-06	0.86	811	0.27	0.36	1.46	1.72E-03	0.007	0.117	836	884
2	20	8.1	1.3	0	10	0.14	0.15	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.563	115	120
2	20	8.1	1.3	5	10	0.14	0.16	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.581	115	120
2	20	8.1	1.3	10	10	0.14	0.16	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.600	115	120
2	20	8.1	1.3	15	10	0.14	0.17	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.618	115	120
2	20	8.1	1.3	20	10	0.14	0.17	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.638	115	120
2	20	8.1	1.3	25	10	0.14	0.18	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.657	115	120
2	20	8.1	1.3	30	10	0.14	0.19	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.676	115	120
2	20	8.1	1.3	35	10	0.14	0.19	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.696	115	120
2	20	8.1	1.3	40	10	0.14	0.20	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.716	115	120
2	20	8.1	1.3	40	0	0	0.20	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.716	115	120
2	20	8.1	1.3	40	10	10	0.20	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.716	115	120
2	20	8.1	1.3	40	20	20	0.20	1.23E-05	4.63E-06	0.86	811	0.03	0.36	0.27	2.34E-04	0.053	0.716	115	120

Table 4.3. Sensitivity of H₂S emissions with respect to air and liquid film thicknesses for each MTCR Model. The following model parameters were held constant: air temperature (19°C), wind speed (1.3 m s⁻¹), ambient H₂S concentration (10 µg m⁻³).

Lagoon Temperature T _L	pH	Liquid film thickness t _L	Air film thickness t _a	Henry's Law Constant H	MTCR (pH constant) H ₂ S Flux J	MTCR (pH gradient) H ₂ S Flux J
°C		cm	cm	(M) _a /(M) _L	µg m ⁻² min ⁻¹	µg m ⁻² min ⁻¹
5	7	0.007	0.912	0.249	949	963
5	7	0.047	0.912	0.249	145	146
5	7	0.086	0.912	0.249	80	80
15	7	0.007	0.912	0.323	1209	1246
15	7	0.047	0.912	0.323	187	190
15	7	0.086	0.912	0.323	103	104
25	7	0.007	0.912	0.401	1472	1549
25	7	0.047	0.912	0.401	232	236
25	7	0.086	0.912	0.401	127	129
5	7	0.047	0.117	0.249	146	147
5	7	0.047	0.912	0.249	145	146
5	7	0.047	1.708	0.249	145	146
15	7	0.047	0.117	0.323	189	190
15	7	0.047	0.912	0.323	187	190
15	7	0.047	1.708	0.323	186	189
25	7	0.047	0.117	0.401	234	237
25	7	0.047	0.912	0.401	232	236
25	7	0.047	1.708	0.401	230	235
5	7.5	0.007	0.912	0.249	718	745
5	7.5	0.047	0.912	0.249	111	113
5	7.5	0.086	0.912	0.249	61	62
15	7.5	0.007	0.912	0.323	900	961
15	7.5	0.047	0.912	0.323	143	146
15	7.5	0.086	0.912	0.323	78	80
25	7.5	0.007	0.912	0.401	1083	1201
25	7.5	0.047	0.912	0.401	177	183
25	7.5	0.086	0.912	0.401	98	100
5	7.5	0.047	0.117	0.249	112	114
5	7.5	0.047	0.912	0.249	111	113
5	7.5	0.047	1.708	0.249	111	113
15	7.5	0.047	0.117	0.323	144	147
15	7.5	0.047	0.912	0.323	143	146
15	7.5	0.047	1.708	0.323	141	146
25	7.5	0.047	0.117	0.401	180	184
25	7.5	0.047	0.912	0.401	177	183
25	7.5	0.047	1.708	0.401	174	182
5	8	0.007	0.912	0.249	548	598
5	8	0.047	0.912	0.249	88	91
5	8	0.086	0.912	0.249	48	50
15	8	0.007	0.912	0.323	682	793
15	8	0.047	0.912	0.323	115	121

Table 4.3. (cont). Sensitivity of H₂S emissions with respect to air and liquid film thicknesses for each MTCR Model. The following model parameters were held constant: air temperature (19°C), wind speed (1.3 m s⁻¹), ambient H₂S concentration (10 µg m⁻³).

15	8	0.086	0.912	0.323	64	66
25	8	0.007	0.912	0.401	802	1019
25	8	0.047	0.912	0.401	146	155
25	8	0.086	0.912	0.401	81	85
5	8	0.047	0.117	0.249	89	91
5	8	0.047	0.912	0.249	88	91
5	8	0.047	1.708	0.249	87	91
15	8	0.047	0.117	0.323	118	121
15	8	0.047	0.912	0.323	115	121
15	8	0.047	1.708	0.323	113	120
25	8	0.047	0.117	0.401	151	156
25	8	0.047	0.912	0.401	146	155
25	8	0.047	1.708	0.401	141	155

Table 4.4. Modeled flux values for the data collected on June 17, 2005 during the summer experimental period.

Time	Sulfide mg L ⁻¹	Lagoon Temp °C	pH	Wind Speed m s ⁻¹	Air Temp (2m) °C	Measured $\mu\text{g m}^{-2} \text{min}^{-1}$	Modeled Results		
							MTNCR	MTCR (pH constant) $\mu\text{g m}^{-2} \text{min}^{-1}$	MTCR (pH gradient)
12:00 AM	4	29.9	8.0	0.4	20.7	11.9	40	231	242
1:00 AM	4	29.5	8.0	1.2	21.6	11.9	40	233	242
2:00 AM	4	29.2	8.0	1.4	22.4	9.2	39	233	242
3:00 AM	4	28.9	8.0	1.0	21.0	9.2	39	232	241
4:00 AM	4	28.7	8.0	1.0	20.1	10.2	39	232	242
5:00 AM	4	28.5	8.0	1.0	19.9	11.8	40	233	242
6:00 AM	4	28.2	8.0	0.6	19.4	12.0	39	232	241
7:00 AM	4	28.1	8.0	1.2	20.4	10.0	40	233	242
8:00 AM	4	28.0	8.0	1.8	21.6	7.6	39	233	241
9:00 AM	4	27.9	8.0	2.0	22.6	6.6	36	231	240
10:00 AM	4	28.0	8.1	2.0	23.4	5.6	33	229	238
11:00 AM	4	28.3	8.1	2.3	24.3		32	229	237
12:00 PM	4	28.9	8.1	2.4	25.7	3.6	31	228	236
1:00 PM	4	29.1	8.1	1.6	26.5	3.3	30	227	236
2:00 PM	4	29.1	8.1	1.4	27.1	2.0	30	226	236
3:00 PM	4	29.5	8.1	1.3	27.5	2.9	29	226	235
4:00 PM	4	30.1	8.1	1.2	28.4	2.5	28	225	235
5:00 PM	4	30.2	8.1	1.3	28.4	2.4	27	225	234
6:00 PM	4	30.1	8.1	1.1	27.8	2.0	27	224	234
7:00 PM	4	29.6	8.1	0.6	25.7	1.8	32	226	237
8:00 PM	4	29.1	8.0	0.8	23.6	3.0	36	230	239
9:00 PM	4	28.9	8.0	0.3	21.4	3.6	38	229	240
10:00 PM	4	28.6	8.0	0.1	20.2	4.4	39	229	241
11:00 PM	4	28.4	8.0	0.4	19.3	4.5	40	231	242

Table 4.5. Seasonally averaged measured and modeled flux values.

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

^aSeasonally averaged value

^bSeasonal range

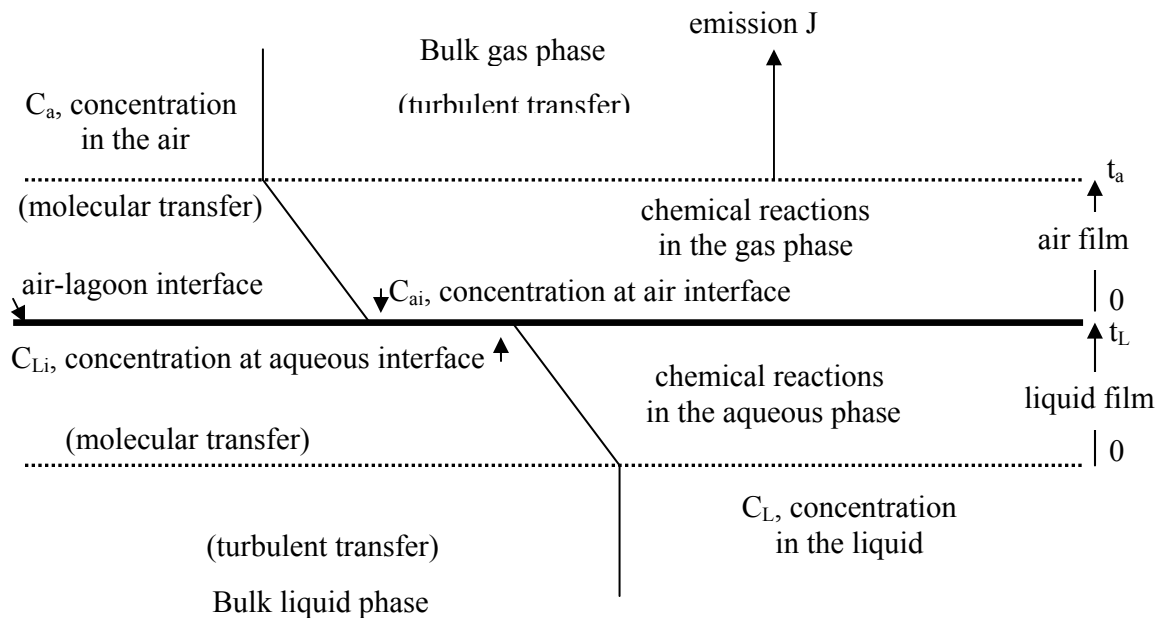


Figure 4.1. Two film theory of mass transfer for the exchange of gases across the gas-liquid system.

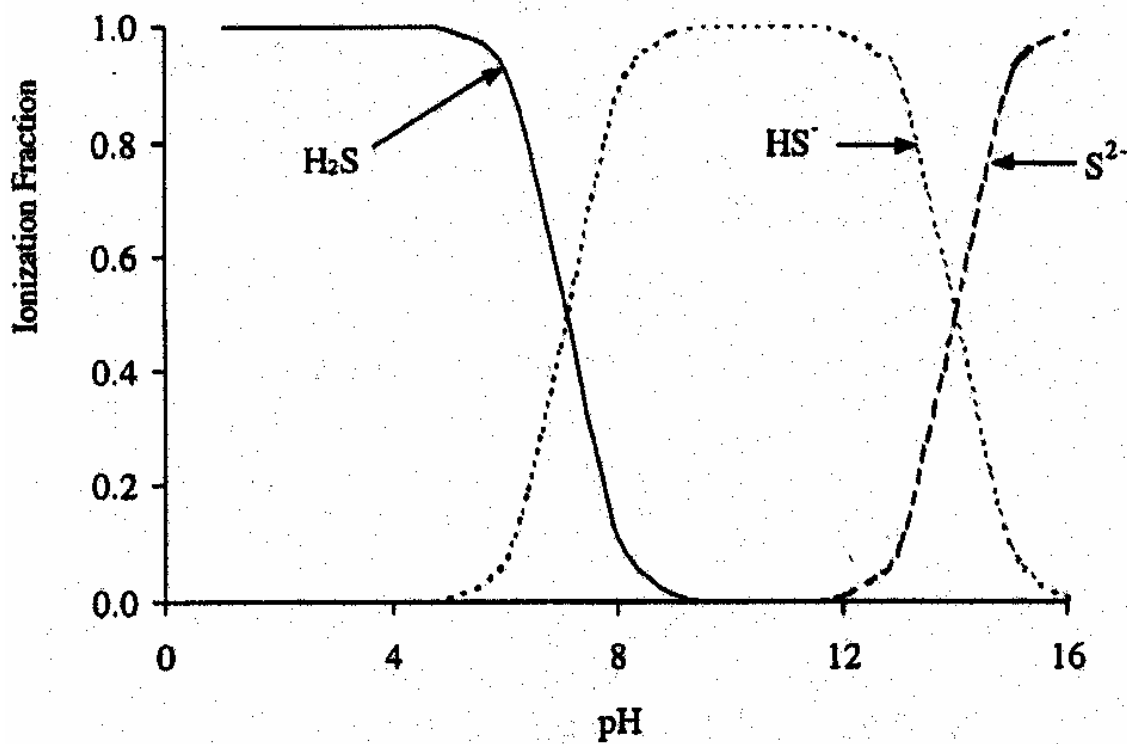


Figure 4.2. Fractions of sulfide species (H_2S , HS^- , S^{2-}) present in aqueous solution as a function of pH at 25°C [Source: Snoeyink and Jenkins (1980)].

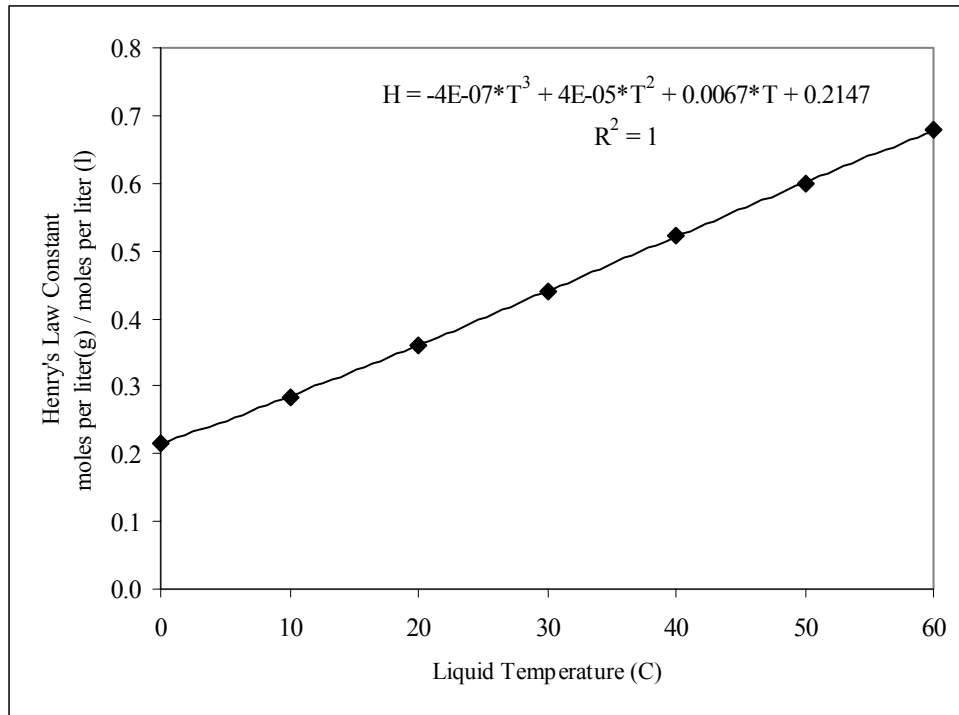


Figure 4.3. Henry's Law Constant graphed as a function of temperature [Data obtained from Metcalf and Eddy (1979)].

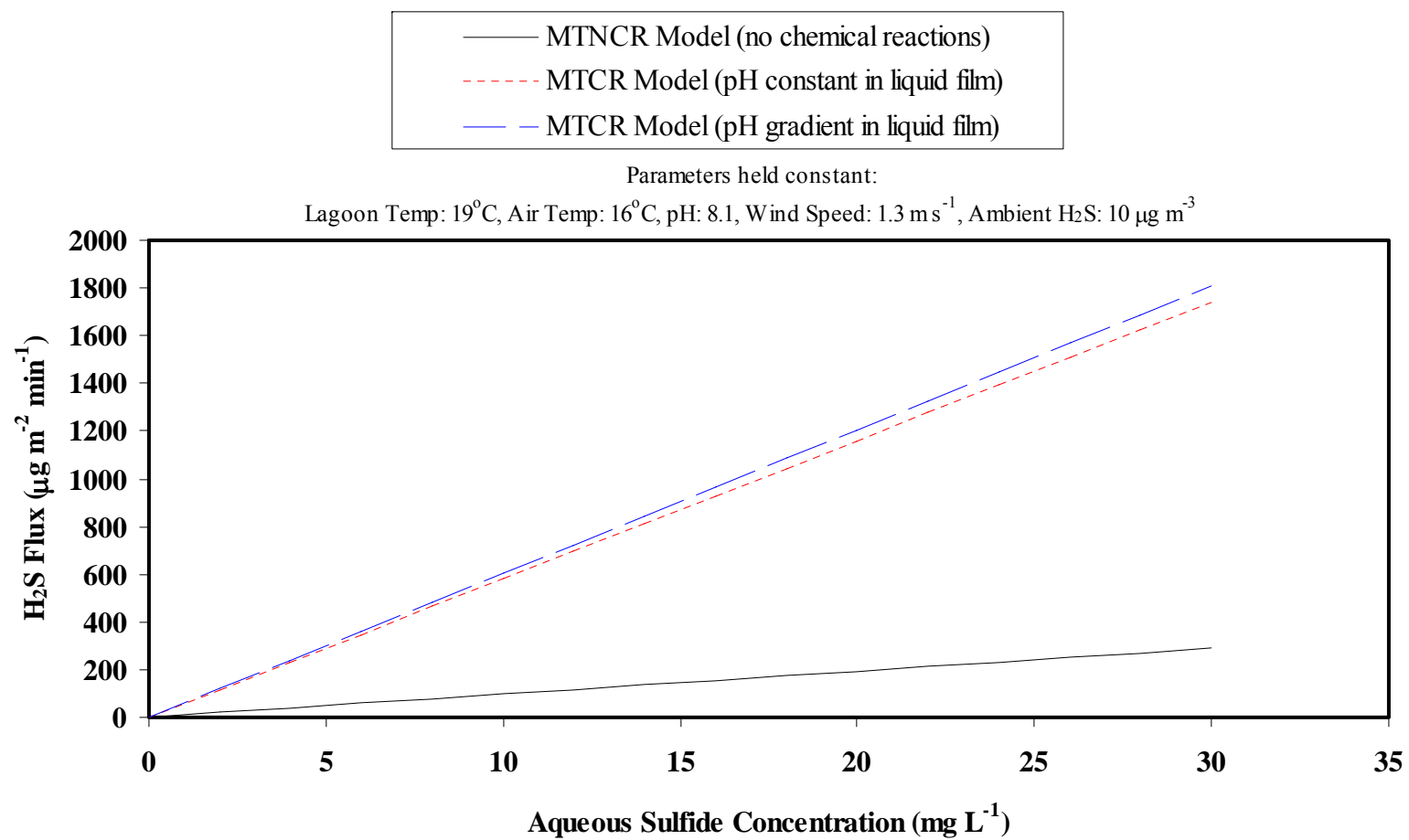


Figure 4.4. Sensitivity of hydrogen sulfide emissions with respect to aqueous sulfide concentration.

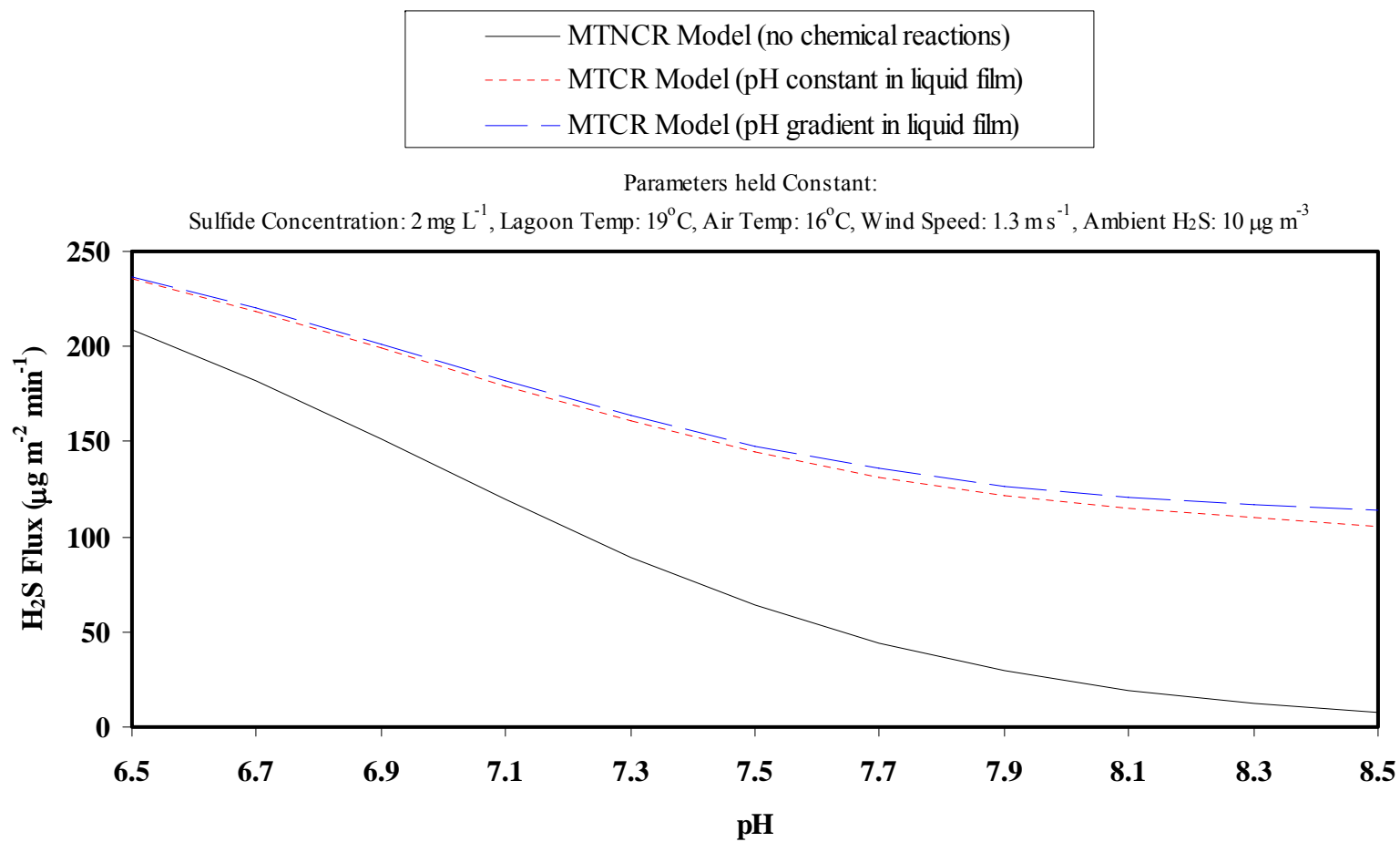


Figure 4.5. Sensitivity of hydrogen sulfide emissions with respect to pH.

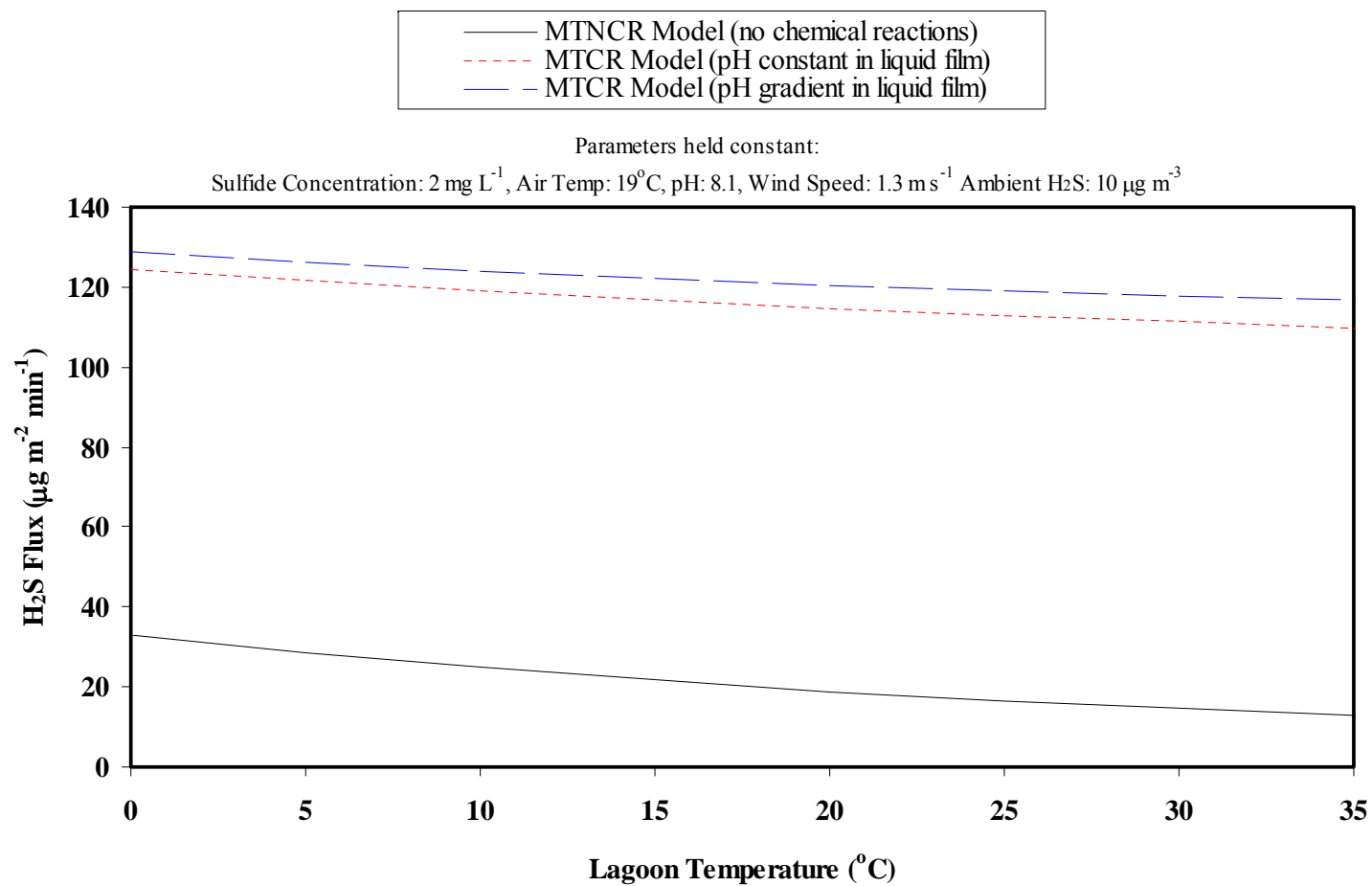
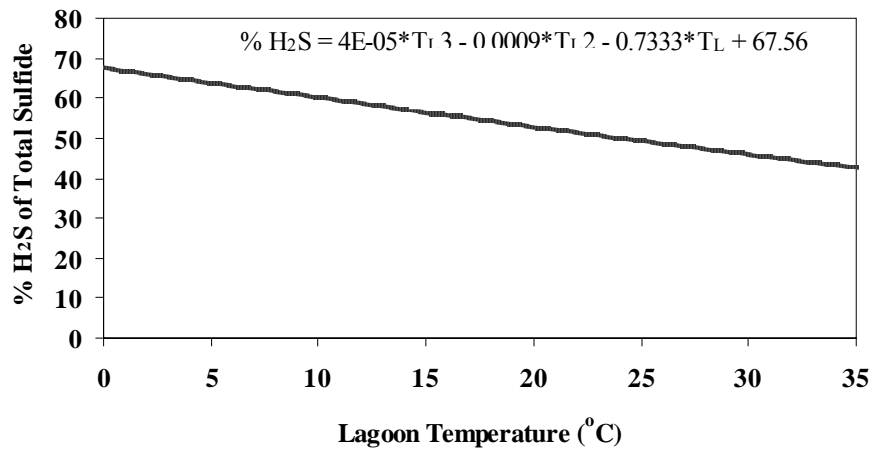
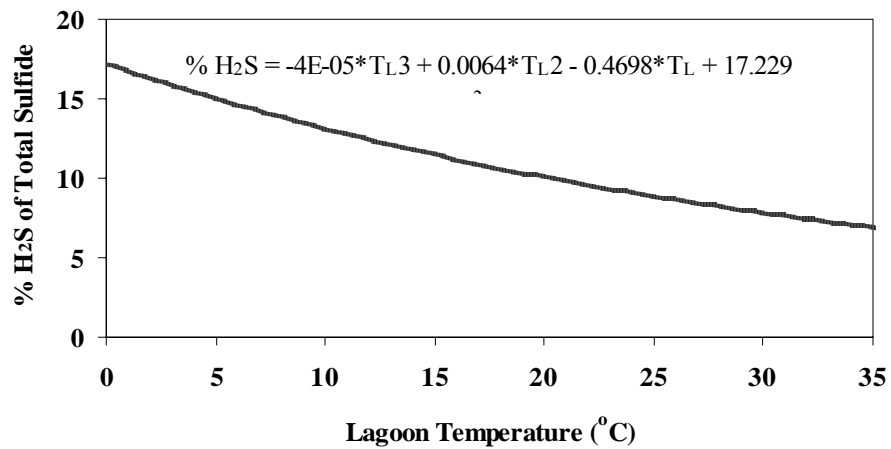


Figure 4.6. Sensitivity of hydrogen sulfide emissions with respect to lagoon temperature.



(a)



(b)

Figure 4.7. Effect of temperature on the fraction of hydrogen sulfide present in total sulfide at (a) pH = 7.0 and (b) pH = 8.0. The temperature dependence on the acidity constant for H_2S and HS^- is calculated using the Van't Hoff Equation [Snoeyink and Jenkins, 1980].

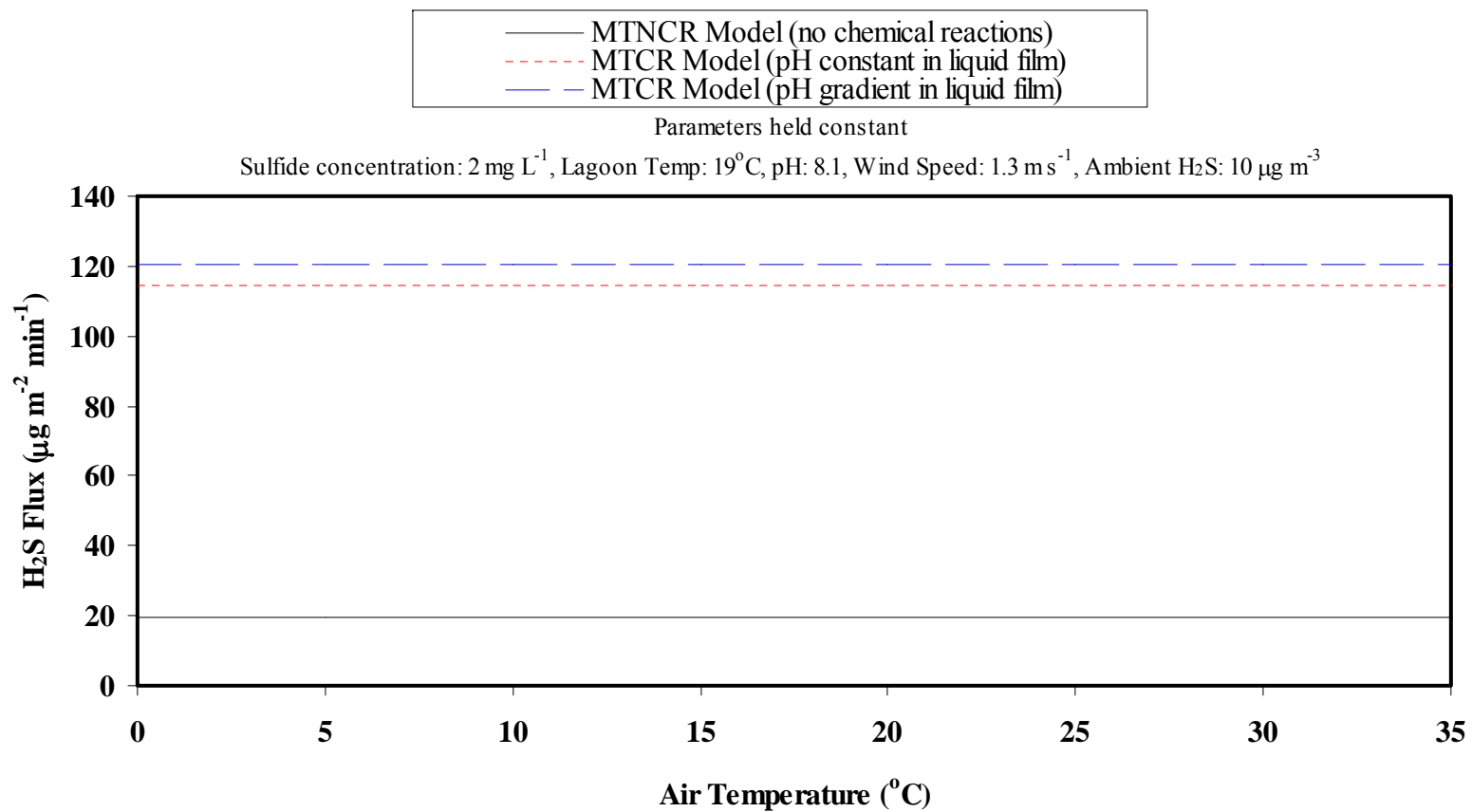


Figure 4.8. Sensitivity of hydrogen sulfide emissions with respect to air temperature.

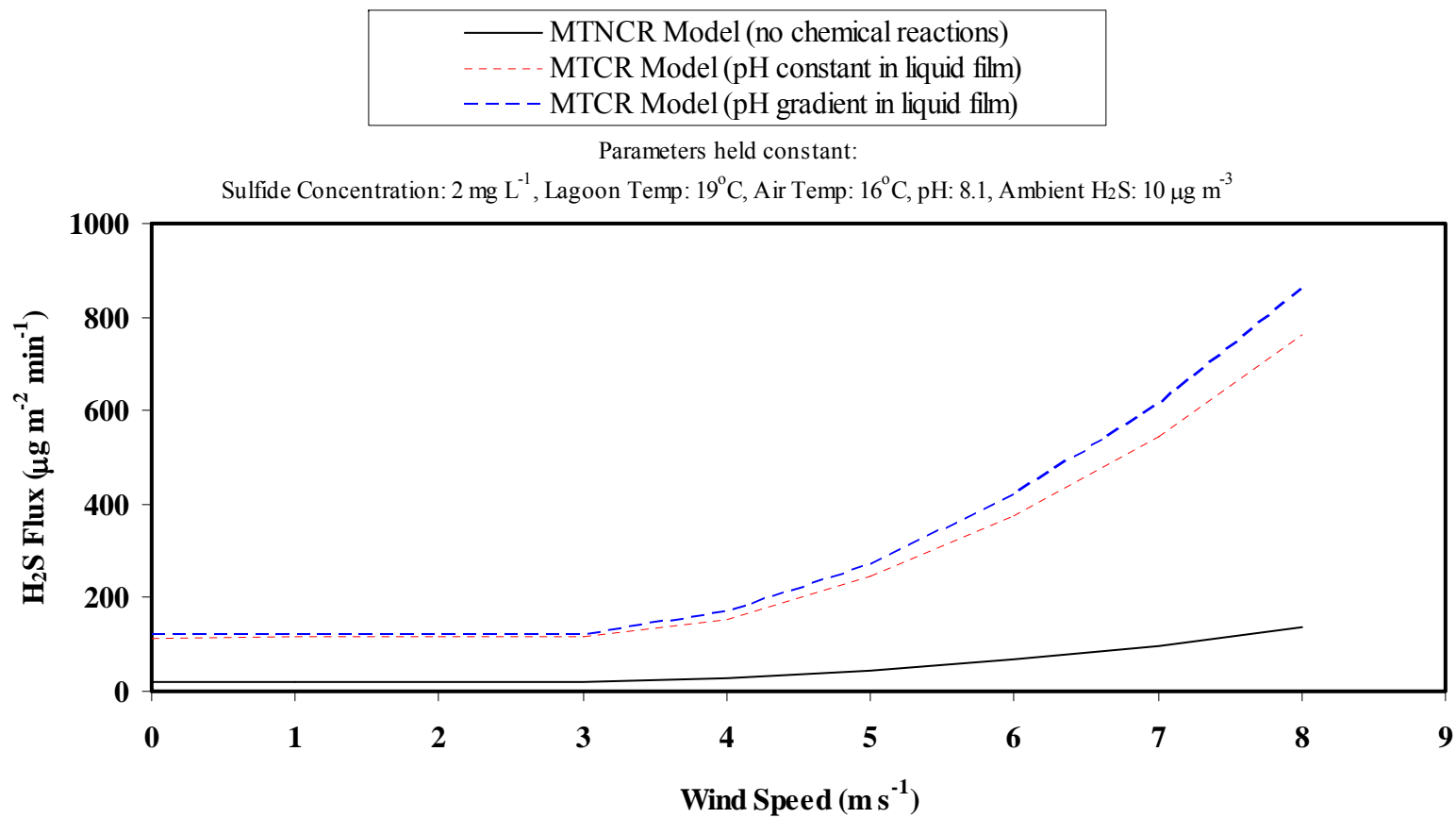


Figure 4.9. Sensitivity of hydrogen sulfide emissions with respect to wind speed.

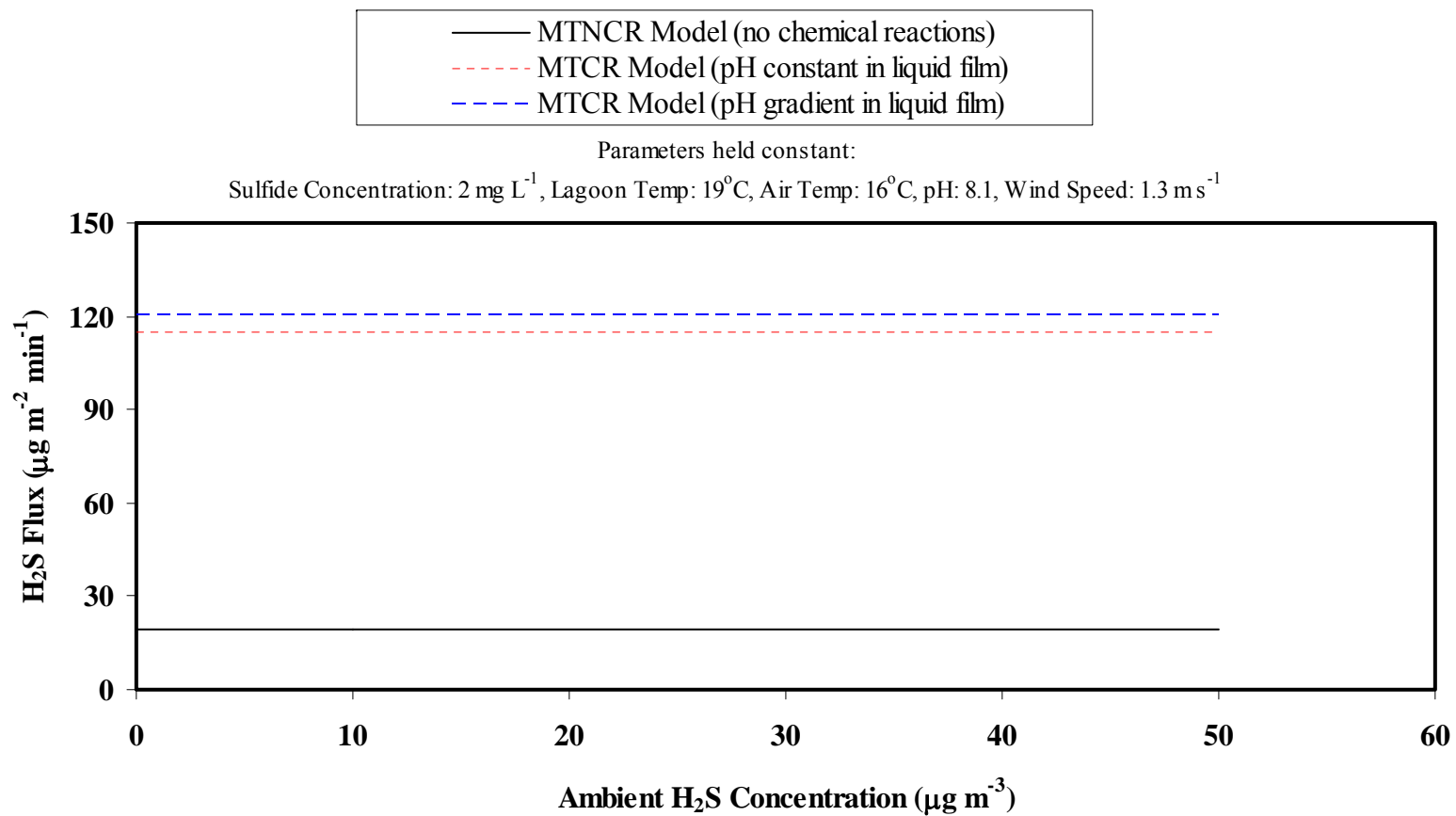


Figure 4.10. Sensitivity of hydrogen sulfide emissions with respect to ambient H₂S concentration.

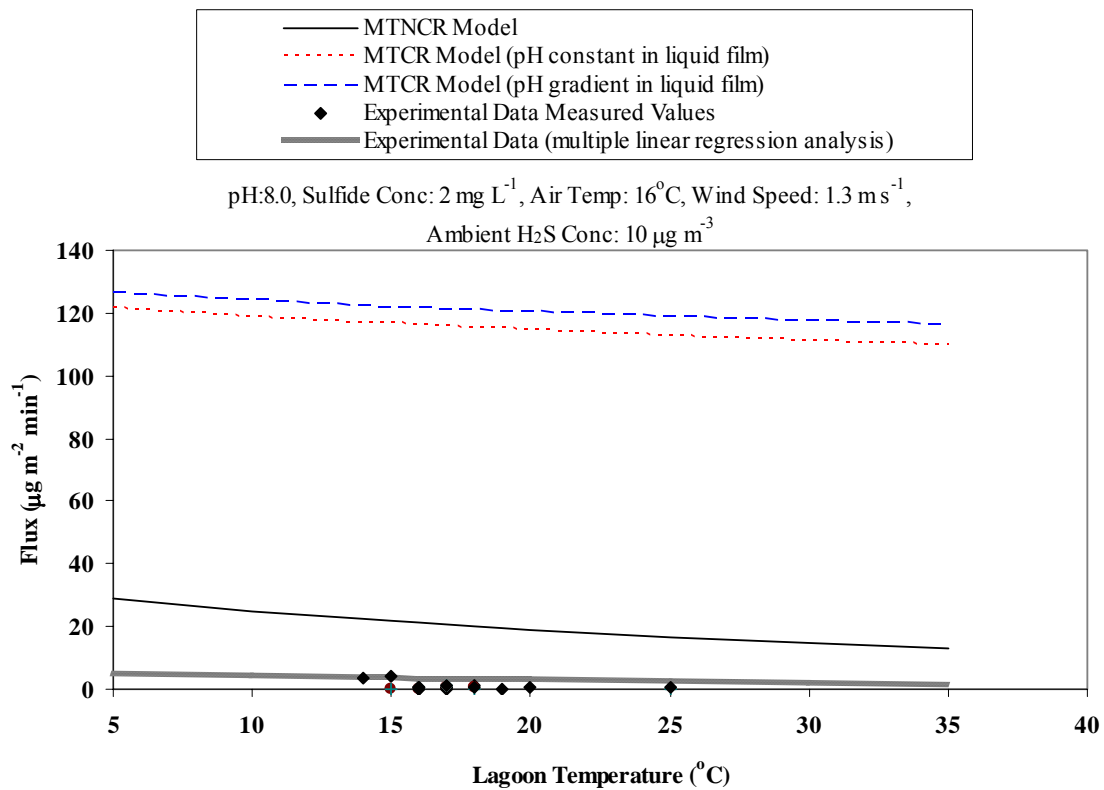


Figure 4.11. Comparison for pH = 8: Modeled hydrogen sulfide flux predictions, flux estimates based on multiple linear regression analysis from three seasonal measurement periods at an experimental site, and measured values within range of modeled conditions. Lagoon temperature, aqueous sulfide concentration, and pH were considered for the multiple linear regression analysis.

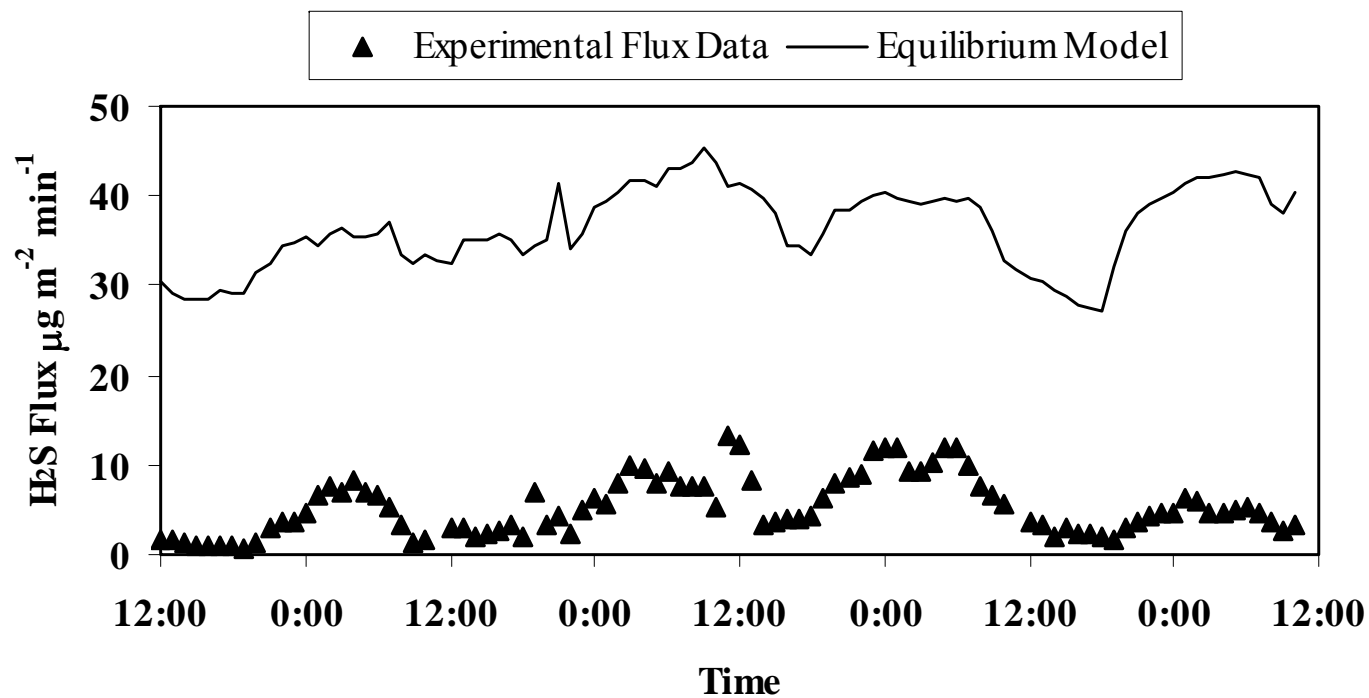


Figure 4.12. Time series comparison of MTNCR Model flux predictions and dynamic flux chamber results for the summer experimental period (June 14-18, 2005).

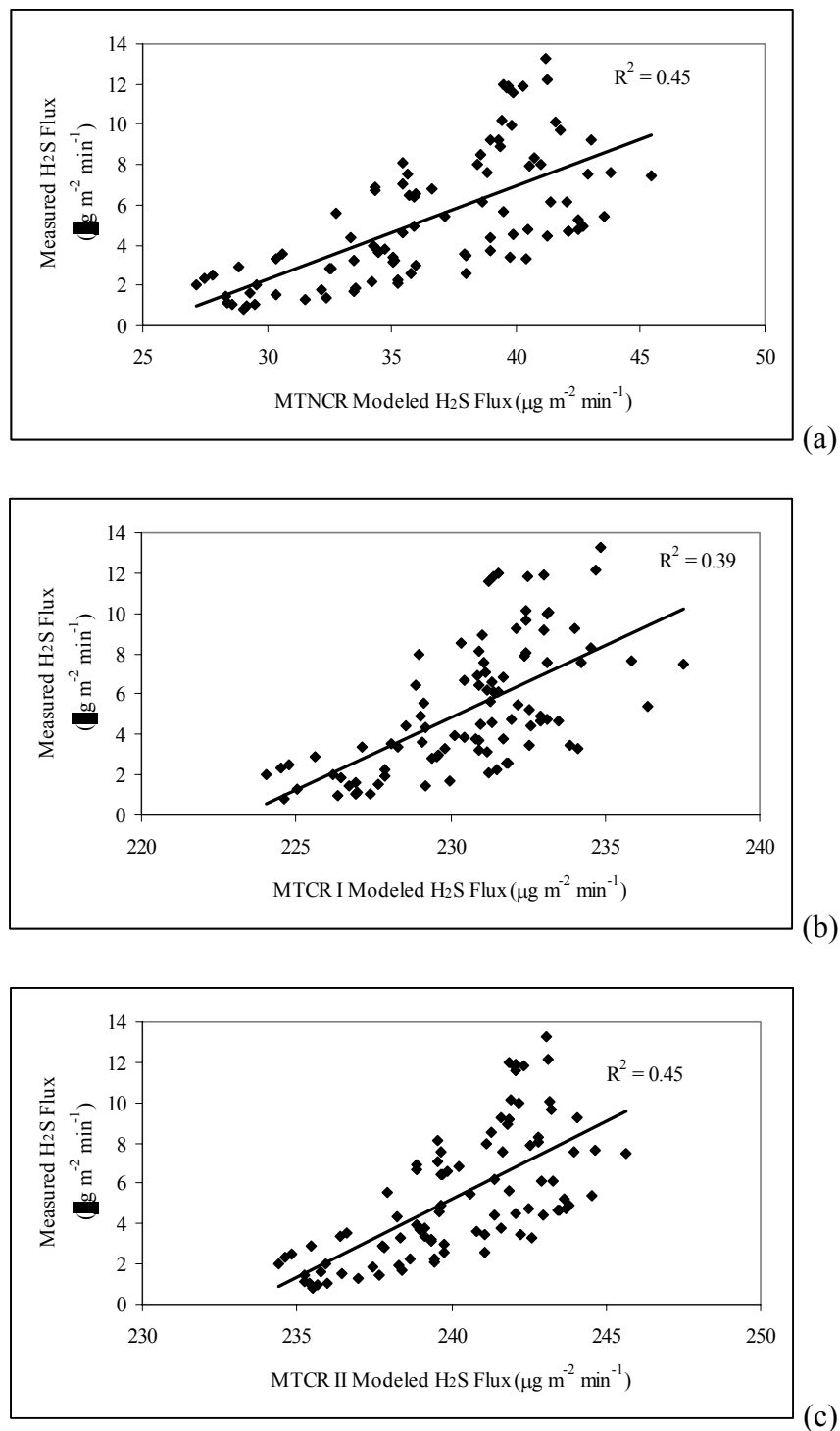


Figure 4.13. Scatter plots of (a) MTNCR, (b) MTCR Model I, and (c) MTCR Model II flux predictions vs dynamic flux chamber results for the summer experimental period (June 14-18, 2005). The hourly averaged diurnal variations are compared and magnitude differences are neglected.

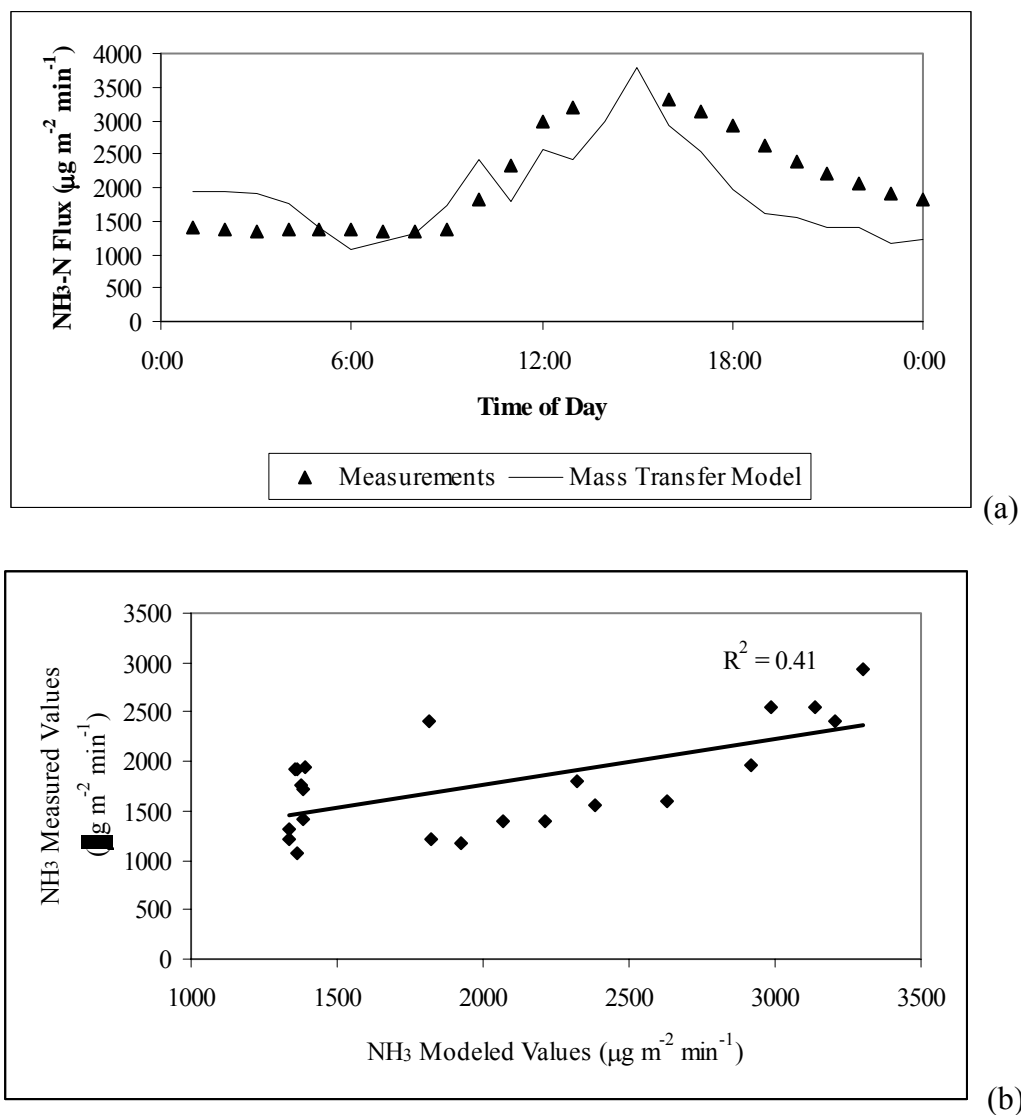


Figure 4.14. (a) 24 hour time series graph of hourly averaged measured ammonia flux (October 31, 2004) versus coupled mass transfer with chemical reactions model (Aneja et al., 2001) predicted values and (b) scatter plot of time series data points to show diurnal trend comparison.

CHAPTER V. SUMMARY AND CONCLUSIONS

An experimental study was conducted at a commercial swine finishing farm in eastern North Carolina to measure hydrogen sulfide emissions from a hog housing unit utilizing a mechanical fan ventilation system and from an on-site waste storage treatment lagoon. A dynamic flow-through chamber system was employed to make lagoon flux measurements. Semi-continuous measurements were made over a one-year period (2004-2005) during the four predominant seasons in order to assess diurnal and temporal variability in emissions as well as the possible influence of meteorological and lagoon parameters. Fan flow rate from the barn was continuously measured in order to accurately assess gaseous emissions from the system. Temperature at the fan outlet and static pressure inside the barn were measured. Lagoon samples were collected daily and analyzed for sulfide content. Lagoon parameters, temperature and pH; and atmospheric environmental parameters, ambient temperature, relative humidity, wind speed, and ambient hydrogen sulfide concentration were concurrently monitored on-site.

At the barn fan outlet, measured H_2S concentrations were highest during the winter and spring, and lowest during the summer, when ventilation rates were higher. The higher concentration values during the winter may be attributed to less airflow through the building compared to other seasons, causing a buildup of the gas to occur. It is likely that the large concentrations measured in the spring are due to the age and weights of the animals housed in the barn. The normalized emission rate from the barn was ~ 3.5 times higher during the winter season than summer, indicating that emissions may not increase linearly with animal mass.

During the lagoon experiments, lowest H₂S fluxes were observed during the winter season and highest flux values were observed during the summer. Hydrogen sulfide emissions were well correlated with lagoon aqueous H₂S concentration, lagoon temperature, and pH. Ambient meteorological parameters, including wind speed and relative humidity, appeared to have much smaller influences over emission rates.

Results from this research initiative are the first reported semi-continuous hydrogen sulfide flux measurements with seasonal and diurnal variability made at swine CAFOs in the southeast U.S. In order to accurately assess statewide H₂S emissions from swine facilities and develop appropriate emission factors, future research is needed at additional CAFOs under various environmental conditions. Furthermore, comparison of emissions using different flux measurement techniques would be useful to corroborate results.

The mechanistic process of H₂S emissions from anaerobic liquid systems are investigated using three different modeling approaches based on the Two-Film theory: coupled Mass Transfer with Chemical Reactions Model with the assumption (1) pH remains constant in the liquid film (MTCR Model I), (2) pH changes from the bulk liquid phase to the air-liquid interface due to diffusion processes that occur within the film (MTCR Model II), and (3) absence of chemical reactions (MTNCR Model). For all models, the hydrogen sulfide flux is dependent on the physico-chemical lagoon parameters, especially sulfide content, 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. Low wind velocities (i.e. $U_{10} < 3.25 \text{ m s}^{-1}$) and air temperature were shown to have little impact on flux. Hydrogen sulfide emissions are

driven primarily by the liquid phase and it was found that varying the liquid film thickness significantly alters flux rates. All three models showed good qualitative agreement in diurnal comparison with flux measurements made at a commercial hog farm during the summer when measured emissions were highest. However, each model significantly over predicted the measured flux rates. Additional field and laboratory measurements would be useful to improve model performance.

While process-based models are both useful and necessary to estimate hydrogen sulfide flux, future research is needed to accurately determine important physical processes such as diffusion and liquid mass transfer coefficients in these types of complex systems that may then be applied to the model. For the models presented in this work, no other chemical lagoon processes are considered that occur in the liquid phase. This lack of information may also significantly affect predicted emission rates. Development of a mechanistic model that incorporates several different lagoon processes would likely enhance flux prediction accuracy.

APPENDICES

Appendix 1. Experimental hourly averaged barn emission rates and meteorological parameters for Winter 2005.

Date	Time	H ₂ S Emission Rate ^a g day ⁻¹ AU ⁻¹	NH ₃ -N Emission Rate ^a g day ⁻¹ AU ⁻¹	H ₂ S conc ^b µg m ⁻³	NH ₃ -N conc ^b µg m ⁻³	Total Fan Flow Rate m ³ min ⁻¹	Barn Temp ^c °C	Ambient Temp ^d °C	RH ^e %
2/22/2005	16:00	4.6	59.1	419	5353	746	23.3	15.7	67
2/22/2005	17:00	5.0	60.1	461	5486	741	23.0	15.6	68
2/22/2005	18:00	4.8	55.4	490	5634	666	22.1	14.4	73
2/22/2005	19:00	4.8	52.6	563	6163	578	22.3	13.1	79
2/22/2005	20:00	5.4	63.6	674	7937	541	22.4	12.5	82
2/22/2005	21:00	4.9	55.6	676	7704	489	22.0	11.3	84
2/22/2005	22:00	5.0	59.6	699	8314	484	22.0	9.5	89
2/22/2005	23:00	5.0	59.7	699	8330	484	21.6	8.4	94
2/22/2005	0:00	5.0	59.7	699	8330	484	21.3	7.9	95
2/23/2005	1:00	5.0	59.7	699	8330	484	20.9	8.1	98
2/23/2005	2:00	5.0	59.7	699	8330	484	21.4	8.4	98
2/23/2005	3:00	5.0	59.7	699	8330	484	21.5	8.3	98
2/23/2005	4:00	5.0	59.7	699	8330	484	21.4	8.1	99
2/23/2005	5:00	5.0	59.7	699	8330	484	21.6	8.7	99
2/23/2005	6:00	5.0	59.7	699	8330	484	21.6	8.6	99
2/23/2005	7:00	5.0	59.7	699	8330	484	21.9	8.7	99
2/23/2005	8:00	5.0	59.7	699	8330	484	22.3	9.0	99
2/23/2005	9:00	5.0	59.7	699	8330	484	22.6	10.1	95
2/23/2005	10:00	4.9	59.7	679	8330	484	22.6	11.2	83
2/23/2005	11:00	3.8	47.6	526	6642	484	22.5	11.1	77
2/23/2005	12:00	3.6	6.6	505	917	484	22.0	10.9	74
2/23/2005	13:00	2.6	60.9	257	5908	694	22.0	12.5	65
2/23/2005	14:00	3.5	77.1	323	7064	738	23.1	14.2	54
2/23/2005	15:00	5.9	73.1	533	6550	754	23.7	15.4	47
2/23/2005	16:00	5.6	61.1	555	6024	687	23.7	15.5	46
2/23/2005	17:00	5.2	53.8	586	6103	596	23.1	15.1	45
2/23/2005	18:00	5.5	52.0	685	6432	547	22.0	13.7	51
2/23/2005	19:00	7.5	58.8	1020	7929	503	22.3	11.2	68
2/23/2005	20:00	8.5	59.7	1186	8330	484	21.9	9.1	73
2/23/2005	21:00	8.7	59.7	1221	8330	484	21.4	8.0	73
2/23/2005	22:00	8.8	59.7	1235	8330	484	20.9	7.2	70
2/23/2005	23:00	8.5	59.6	1188	8317	484	20.1	6.3	68
2/23/2005	0:00	6.3	46.4	1132	8309	377	19.9	5.4	71
2/24/2005	1:00	6.0	42.5	1168	8330	345	20.2	5.4	74
2/24/2005	2:00	6.0	43.4	1157	8330	352	20.1	5.7	72
2/24/2005	3:00	6.5	45.1	1208	8330	366	20.3	6.1	66
2/24/2005	4:00	6.6	47.3	1168	8330	384	20.2	6.7	63
2/24/2005	5:00	6.8	48.6	1164	8330	394	20.5	7.1	67
2/24/2005	6:00	6.6	46.9	1175	8330	381	20.3	6.6	82
2/24/2005	7:00	6.1	45.0	1133	8330	365	20.4	6.1	93
2/24/2005	8:00	6.4	46.1	1149	8330	374	20.6	6.4	96
2/24/2005	9:00	6.5	47.1	1153	8330	382	21.1	6.7	96

Appendix 1 (cont). Experimental hourly averaged barn emission rates and meteorological parameters for Winter 2005.

2/24/2005	10:00	6.6	48.2	1139	8330	391	20.9	7.0	96
2/24/2005	11:00	6.8	49.8	1132	8330	404	21.0	7.4	96
2/24/2005	12:00	7.0	51.7	1126	8330	420	21.5	7.9	96
2/24/2005	13:00	7.3	52.3	1156	8330	424	22.0	8.1	96
2/24/2005	14:00	7.2	53.0	1131	8330	430	22.3	8.3	96
2/24/2005	15:00	7.5	52.1	1199	8330	423	22.2	8.0	96
2/24/2005	16:00	7.2	50.8	1186	8330	413	22.0	7.7	96
2/24/2005	17:00	7.0	48.1	1209	8330	391	21.6	6.9	96
2/24/2005	18:00	6.5	45.0	1210	8330	365	20.9	6.1	96
2/24/2005	19:00	6.2	43.6	1173	8330	354	19.8	5.5	96
2/24/2005	20:00	4.7	33.6	1137	8136	279	19.0	4.7	95
2/24/2005	21:00	4.0	27.3	1157	7992	231	19.4	4.3	94
2/24/2005	22:00	4.0	26.8	1184	7984	227	19.0	4.1	93
2/24/2005	23:00	3.8	26.7	1151	8093	223	19.1	3.9	93
2/24/2005	0:00	3.6	25.8	1113	8047	216	18.1	3.5	92
2/25/2005	1:00	3.5	24.5	1122	7851	211	18.1	3.2	92
2/25/2005	2:00	3.3	23.1	1089	7651	204	17.4	2.7	92
2/25/2005	3:00	3.1	22.2	1071	7574	198	17.6	2.4	92
2/25/2005	4:00	3.1	21.7	1083	7548	194	17.6	2.2	93
2/25/2005	5:00	3.3	21.8	1148	7633	193	17.9	2.1	91
2/25/2005	6:00	3.1	22.2	1109	7828	192	17.6	2.1	91
2/25/2005	7:00	3.2	22.0	1131	7815	190	18.4	1.9	88
2/25/2005	8:00	3.4	21.9	1206	7853	189	18.4	1.8	84
2/25/2005	9:00	3.3	22.6	1166	7997	191	19.0	2.0	83
2/25/2005	10:00	3.0	21.2	1121	8076	178	19.6	2.4	81
2/25/2005	11:00	3.0	24.1	1035	8228	198	19.6	2.4	74
2/25/2005	12:00	3.0	21.0	1071	7545	188	19.0	2.2	76
2/25/2005	13:00	3.6	23.3	1109	7237	218	19.5	2.4	74
2/25/2005	14:00	3.8	25.0	1129	7469	227	20.1	3.0	71
2/25/2005	15:00	4.3	25.5	1164	6923	249	20.4	3.1	69
2/25/2005	16:00	4.1	24.0	1165	6847	237	20.0	3.2	68
2/25/2005	17:00	4.0	23.2	1190	6848	229	20.0	3.5	67
2/25/2005	18:00	3.7	19.7	1186	6273	212	19.5	3.5	68
2/25/2005	19:00	2.6	12.8	1099	5394	161	18.1	2.7	72
2/25/2005	20:00	2.5	9.7	1074	4211	157	17.0	1.3	86
2/25/2005	21:00	2.2	7.5	1038	3531	145	16.4	-0.3	94
2/25/2005	22:00	2.0	6.9	1009	3427	136	15.9	-0.8	97
2/25/2005	23:00	0.7	3.4	397	1840	131	15.3	-1.6	98
2/25/2005	0:00	0.0	1.6	9	817	133	15.5	-2.0	99
2/26/2005	1:00	0.0	1.3	3	735	121	14.6	-2.2	98
2/26/2005	2:00	0.0	1.0	1	562	120	14.7	-2.3	98
2/26/2005	3:00	0.0	0.9	1	538	108	14.0	-2.7	99
2/26/2005	4:00	0.0	0.9	0	523	114	13.9	-3.0	99
2/26/2005	5:00	0.0	0.7	0	431	109	13.8	-3.2	99
2/26/2005	6:00	0.0	0.6	0	414	106	13.7	-3.0	99
2/26/2005	7:00	0.0	0.7	0	386	121	14.6	-3.2	99
2/26/2005	8:00	0.0	0.9	1	488	128	15.1	-2.4	98
2/26/2005	9:00	0.1	4.4	40	1513	179	18.3	0.9	86

Appendix 1 (cont). Experimental hourly averaged barn emission rates and meteorological parameters for Winter 2005.

2/26/2005	10:00	3.1	20.0	917	5939	226	19.6	3.4	73
2/26/2005	11:00	4.0	27.1	1060	6524	247	20.1	5.4	60
2/26/2005	12:00			642	6458	247	21.1	7.2	53
2/26/2005	13:00			231	8330	301	21.6	8.4	50
2/26/2005	14:00			76	8330	374	21.6	9.4	48
2/26/2005	15:00	2.6	46.9	280	8331	412	21.4	10.2	45
2/26/2005	16:00	2.5	49.6	417	8330	403	21.7	10.9	42
2/26/2005	17:00	4.5	45.2	864	8330	367	22.0	11.3	39
2/26/2005	18:00	4.8	32.1	1207	8054	269	22.3	10.2	43
2/26/2005	19:00	4.9	17.1	1326	4678	248	20.8	6.9	71
2/26/2005	20:00	3.9	11.4	1247	3641	212	19.4	4.1	82
2/26/2005	21:00	3.1	8.5	1195	3276	175	18.6	3.1	90
2/26/2005	22:00	3.1	7.9	1203	3088	174	18.1	2.3	92
2/26/2005	23:00	3.0	7.9	1159	3041	176	17.4	1.4	94
2/26/2005	0:00	2.8	7.5	1186	3215	159	17.4	0.8	97
2/27/2005	1:00	2.7	8.3	1155	3577	157	17.3	1.1	97
2/27/2005	2:00	2.4	6.8	1132	3223	143	16.7	0.1	97
2/27/2005	3:00	2.7	6.6	1192	2948	151	17.2	0.0	98
2/27/2005	4:00	2.3	6.0	1085	2857	142	16.7	-0.2	98
2/27/2005	5:00	2.4	5.9	1117	2772	145	16.8	0.1	99
2/27/2005	6:00	2.3	5.7	1073	2692	143	16.7	-0.1	99
2/27/2005	7:00	2.6	6.6	1126	2843	158	17.1	-0.1	99
2/27/2005	8:00	2.7	7.3	1088	2905	170	17.7	0.7	99
2/27/2005	9:00	3.5	11.4	1165	3788	200	18.9	2.0	97
2/27/2005	10:00	3.6	17.6	1179	5809	204	19.2	4.2	87
2/27/2005	11:00	4.5	29.0	1227	7883	249	20.4	6.2	73
2/27/2005	12:00	4.4	30.6	1201	8330	248	21.9	8.0	60

^a AU = Animal Unit (500 kg)

^b Concentration measured at 91cm fan outlet

^c Measured at 91 cm fan outlet

^d Measured at 2m height above surface

^e RH = Relative Humidity in ambient air

Appendix 2. Experimental hourly averaged barn emission rates and meteorological parameters for Spring 2005.

Date	Time	H ₂ S Emission Rate ^a g day ⁻¹ AU ⁻¹	NH ₃ -N Emission Rate ^a g day ⁻¹ AU ⁻¹	H ₂ S conc ^b µg m ⁻³	NH ₃ -N conc ^b µg m ⁻³	Total Fan Flow Rate m ³ min ⁻¹	Barn Temp ^c Celcius	Ambient Temp ^d Celcius	RH ^e %
4/7/2005	14:00	2.4	32.6	163	2253	1483	26.5	23.6	61
4/7/2005	15:00	1.8	36.2	126	2517	1476	26.0	22.7	66
4/7/2005	16:00	1.3	36.4	92	2541	1469	25.2	22.0	70
4/7/2005	17:00	1.4	36.3	98	2555	1459	25.0	21.9	71
4/7/2005	18:00	1.8	35.3	199	3804	952	25.6	20.8	75
4/7/2005	19:00	2.3	37.1	250	4016	948	25.1	19.9	82
4/7/2005	20:00	2.7	34.8	298	3778	944	24.2	18.6	90
4/7/2005	21:00	3.1	33.6	335	3641	947	23.8	18.4	90
4/7/2005	22:00	3.3	33.6	359	3651	945	23.6	17.8	92
4/7/2005	23:00	2.9	31.8	318	3446	948	23.9	18.3	93
4/7/2005	0:00	3.0	33.0	326	3576	946	24.0	18.6	91
4/8/2005	1:00	3.2	32.9	341	3557	949	24.1	18.7	92
4/8/2005	2:00	3.4	32.5	366	3499	953	23.9	18.6	91
4/8/2005	3:00	3.4	31.5	379	3484	927	23.5	18.0	91
4/8/2005	4:00	4.0	32.3	492	3884	861	23.8	17.4	92
4/8/2005	5:00	4.3	32.2	584	4277	770	24.2	16.5	96
4/8/2005	6:00	3.9	30.0	559	4169	741	24.2	16.8	95
4/8/2005	7:00	3.8	38.9	420	4278	933	23.7	17.5	94
4/8/2005	8:00	3.7	38.1	399	4142	944	23.6	16.9	95
4/8/2005	9:00	4.4	42.3	477	4591	947	23.8	16.9	95
4/8/2005	10:00	3.4	39.2	363	4142	970	23.9	17.5	92
4/8/2005	11:00	3.0	41.0	310	4316	976	26.0	20.3	79
4/8/2005	12:00	2.0	50.6	135	3457	1501	25.6	22.6	66
4/8/2005	13:00	1.4	39.5	100	2739	1478	26.6	23.6	59
4/8/2005	14:00	1.4	35.7	97	2535	1446	26.6	23.5	55
4/8/2005	15:00	1.6	37.5	112	2649	1453	26.8	23.6	55
4/8/2005	16:00	2.0	40.1	142	2861	1438	26.2	22.9	60
4/8/2005	17:00	1.8	42.4	126	3030	1437	26.0	23.0	62
4/8/2005	18:00	2.4	47.8	184	3663	1340	25.6	22.3	65
4/8/2005	19:00	3.4	46.5	384	5210	915	24.9	19.7	77
4/8/2005	20:00	3.5	33.9	398	3803	916	23.9	18.2	85
4/8/2005	21:00	3.8	33.2	423	3722	916	23.8	17.9	86
4/8/2005	22:00	3.8	32.8	431	3691	913	23.5	17.4	87
4/8/2005	23:00	3.8	31.8	497	4047	819	23.5	16.9	88
4/8/2005	0:00	3.9	30.1	664	5086	616	24.3	16.0	93
4/9/2005	1:00	3.7	27.8	731	5509	518	24.5	15.7	96
4/9/2005	2:00	3.9	30.0	767	5952	517	24.0	14.7	95
4/9/2005	3:00	4.0	30.6	782	5976	525	22.9	13.2	95
4/9/2005	4:00	3.8	29.2	760	5902	507	22.2	12.4	96
4/9/2005	5:00	3.7	29.8	737	5941	515	21.7	12.2	94
4/9/2005	6:00	3.8	31.9	746	6246	524	21.8	12.0	96
4/9/2005	7:00	3.8	34.6	779	7010	506	22.7	12.3	96

Appendix 2 (cont). Experimental hourly averaged barn emission rates and meteorological parameters for Spring 2005.

4/9/2005	8:00	3.9	37.4	760	7332	524	22.6	12.5	94
4/9/2005	9:00	3.7	35.7	732	7018	521	22.5	12.6	90
4/9/2005	10:00	3.4	33.8	699	7023	494	23.3	13.7	81
4/9/2005	11:00	3.1	33.5	654	6999	528	23.7	14.7	75
4/9/2005	12:00					644	23.6	15.2	72
4/9/2005	13:00			172	6047	928	24.1	17.5	60
4/9/2005	14:00			214	5108	916	24.6	18.3	47
4/9/2005	15:00	1.6	39.7	167	4207	1058	23.5	18.8	39
4/9/2005	16:00	2.2	39.3	211	3791	1069	22.7	18.4	31
4/9/2005	17:00	3.0	49.9	328	5410	955	22.7	17.7	30
4/9/2005	18:00	4.0	55.4	454	6239	911	22.0	16.5	32
4/9/2005	19:00	4.4	43.9	494	4955	909	20.3	14.4	38
4/9/2005	20:00	4.1	34.6	523	4404	805	18.6	12.5	46
4/9/2005	21:00	3.3	26.3	601	4758	568	18.4	11.4	49
4/9/2005	22:00	3.3	25.2	684	5228	496	18.0	9.7	59
4/9/2005	23:00	3.4	26.8	713	5540	496	17.6	7.7	75
4/9/2005	0:00	3.3	25.7	679	5320	496	17.1	7.9	70
4/10/2005	1:00	3.4	25.4	694	5257	496	17.2	7.3	73
4/10/2005	2:00	2.9	23.2	599	4789	497	15.9	6.9	73
4/10/2005	3:00	2.9	22.3	610	4659	490	15.8	6.4	70
4/10/2005	4:00	2.6	20.0	592	4570	449	15.2	6.0	74
4/10/2005	5:00	2.5	19.5	598	4613	434	15.1	5.7	76
4/10/2005	6:00	2.4	19.8	538	4495	452	14.8	5.7	76
4/10/2005	7:00	2.3	21.8	506	4680	478	15.7	6.8	71
4/10/2005	8:00	2.4	24.5	501	5066	496	17.7	9.6	59
4/10/2005	9:00	2.8	38.5	386	5153	774	19.0	12.5	46
4/10/2005	10:00	2.8	40.6	362	5180	810	21.7	14.3	37
4/10/2005	11:00	2.2	49.5	259	5696	894	23.7	16.4	32
4/10/2005	12:00	1.5	44.3	164	4957	916	24.8	18.1	27
4/10/2005	13:00	1.1	43.0	126	4814	916	26.0	19.6	27
4/10/2005	14:00	1.9	69.9	155	5967	1206	25.8	20.5	25
4/10/2005	15:00	4.0	48.0	306	3763	1331	25.6	21.4	23
4/10/2005	16:00	4.1	42.4	319	3221	1362	25.7	21.7	23
4/10/2005	17:00	4.2	42.6	301	3054	1431	25.3	22.0	23
4/10/2005	18:00	3.1	31.8	356	3614	902	25.7	21.5	23
4/10/2005	19:00	3.0	32.7	424	4504	778	24.0	18.1	40
4/10/2005	20:00	3.5	31.2	669	5911	546	22.9	13.8	60
4/10/2005	21:00	3.1	26.2	677	5624	476	21.5	11.1	78
4/10/2005	22:00	3.2	25.1	712	5595	460	20.5	9.7	85
4/10/2005	23:00	3.2	24.4	800	6046	415	20.4	8.2	85
4/10/2005	0:00	3.2	22.6	855	5999	386	19.9	7.3	89
4/11/2005	1:00	3.0	21.6	874	6252	356	19.8	6.0	90
4/11/2005	2:00	3.0	20.2	903	6167	336	19.3	5.2	93
4/11/2005	3:00	3.0	19.4	948	6235	319	19.5	4.8	94
4/11/2005	4:00	2.8	18.2	966	6257	298	19.9	4.5	95
4/11/2005	5:00	2.8	19.0	998	6759	289	19.5	4.0	96
4/11/2005	6:00	2.8	19.7	912	6484	312	19.6	4.0	97
4/11/2005	7:00	2.5	23.1	745	6757	351	19.5	5.6	96

Appendix 2 (cont). Experimental hourly averaged barn emission rates and meteorological parameters for Spring 2005.

4/11/2005	8:00	1.9	31.7	436	7048	461	21.2	11.1	73
4/11/2005	9:00	1.3	42.5	227	6818	643	23.3	17.0	46
4/11/2005	10:00	0.8	60.9	79	6838	922	25.2	20.0	34
4/11/2005	11:00			11	6454	1329	25.4	21.6	29
4/11/2005	12:00			-15	4840	1460	26.0	23.2	27
4/11/2005	13:00			-7	5176	1447	27.1	24.2	26
4/11/2005	14:00	2.8	63.9	210	4099	1605	27.6	25.1	25
4/11/2005	15:00	2.5	50.3	129	2614	1975	27.4	26.2	25
4/11/2005	16:00	2.5	37.7	132	1980	1951	27.4	26.7	25
4/11/2005	17:00	2.4	35.9	126	1903	1937	27.0	26.4	25
4/11/2005	18:00	2.1	34.3	142	2407	1519	26.0	23.7	29
4/11/2005	19:00	2.0	33.1	227	3784	899	24.8	20.1	32
4/11/2005	20:00	2.5	31.4	334	4128	797	23.6	17.9	36
4/11/2005	21:00	3.2	35.4	460	5121	710	23.6	16.0	51
4/11/2005	22:00	2.7	28.6	565	5989	491	23.6	14.0	75
4/11/2005	23:00	2.9	31.9	563	6171	532	23.0	12.4	78
4/11/2005	0:00	2.7	29.4	554	6115	493	22.3	11.0	80
4/12/2005	1:00	2.4	28.4	496	5911	493	21.6	10.4	84
4/12/2005	2:00	2.4	28.8	505	5989	493	20.7	9.6	88
4/12/2005	3:00	2.5	27.2	539	5883	475	20.8	9.1	92
4/12/2005	4:00	2.4	27.9	500	5798	493	20.2	8.9	93
4/12/2005	5:00	2.3	27.8	474	5796	492	20.6	9.3	93
4/12/2005	6:00	2.1	29.2	448	6083	492	20.4	9.6	92
4/12/2005	7:00	2.1	30.4	445	6332	492	21.3	10.0	91
4/12/2005	8:00	2.0	32.8	424	6830	492	21.8	11.0	89
4/12/2005	9:00	2.1	34.1	447	7116	492	22.3	11.7	87
4/12/2005	10:00	2.1	36.1	434	7528	492	23.4	13.4	82
4/12/2005	11:00					492	23.7	14.4	76
4/12/2005	12:00	3.0	50.0	370	6642	648	23.6	14.8	76
4/12/2005	13:00	3.7	44.6	529	6210	738	24.0	15.3	70
4/12/2005	14:00	4.7	48.8	573	5883	852	23.5	14.6	63
4/12/2005	15:00	4.6	42.7	676	6136	716	23.6	14.2	58
4/12/2005	16:00	4.7	45.1	747	7005	662	23.9	14.0	59
4/12/2005	17:00	4.6	43.2	789	7233	616	23.7	13.3	65
4/12/2005	18:00	4.2	34.9	880	7293	491	23.1	12.3	76
4/12/2005	19:00	4.1	33.7	848	7039	491	22.3	11.5	86
4/12/2005	20:00	4.0	33.6	834	7014	492	21.7	10.9	92
4/12/2005	21:00	3.9	31.4	811	6542	492	21.4	11.0	93
4/12/2005	22:00	3.9	32.0	821	6677	492	21.6	10.6	96
4/12/2005	23:00	3.8	31.9	794	6647	493	21.3	10.6	97
4/12/2005	0:00	3.7	31.1	781	6479	493	21.4	10.5	97
4/13/2005	1:00	3.8	31.4	800	6548	493	21.2	10.2	98
4/13/2005	2:00	3.8	30.0	792	6245	493	20.7	9.5	98
4/13/2005	3:00	3.9	24.7	803	5132	493	20.3	9.6	98
4/13/2005	4:00	4.4	17.8	920	3708	493	20.9	9.9	98
4/13/2005	5:00	4.3	18.6	906	3871	493	21.4	10.3	98
4/13/2005	6:00	4.4	19.5	917	4066	492	21.6	10.6	98
4/13/2005	7:00	4.3	21.0	906	4375	492	21.7	10.5	97

Appendix 2 (cont). Experimental hourly averaged barn emission rates and meteorological parameters for Spring 2005.

4/13/2005	8:00	4.2	19.5	884	4072	492	21.0	9.9	97
4/13/2005	9:00	4.1	19.7	857	4114	491	20.8	10.1	97
4/13/2005	10:00	4.5	20.7	932	4310	492	22.1	10.4	97
4/13/2005	11:00	4.2	22.0	883	4582	493	21.3	10.6	96
4/13/2005	12:00	4.0	22.1	826	4607	493	20.9	10.5	95
4/13/2005	13:00	4.1	19.7	858	4098	493	21.2	10.4	95
4/13/2005	14:00	4.3	20.5	893	4282	492	21.8	10.7	95
4/13/2005	15:00	4.2	20.1	874	4185	492	21.3	10.2	95
4/13/2005	16:00	4.4	19.8	926	4134	493	21.6	9.5	96
4/13/2005	17:00	4.5	18.0	936	3759	493	21.3	9.3	96
4/13/2005	18:00	4.4	17.5	958	3772	478	20.7	8.9	96
4/13/2005	19:00	4.3	15.3	1025	3670	427	20.6	8.2	96
4/13/2005	20:00	3.9	12.3	1151	3575	352	19.8	7.1	92
4/13/2005	21:00	4.0	11.9	1127	3377	361	19.3	6.0	88
4/13/2005	22:00	3.9	12.5	1115	3542	362	18.9	5.9	90
4/13/2005	23:00	4.0	12.1	1133	3405	365	19.5	6.0	94
4/13/2005	0:00	3.9	12.0	1110	3389	363	19.0	5.7	95
4/14/2005	1:00	3.8	13.8	1078	3886	364	18.8	5.7	94
4/14/2005	2:00	3.9	12.4	1135	3636	349	19.4	5.8	92
4/14/2005	3:00	3.8	12.6	1130	3751	343	19.3	5.9	86
4/14/2005	4:00	3.9	13.4	1088	3775	365	18.8	5.7	87
4/14/2005	5:00	3.7	12.2	1075	3580	349	19.1	5.8	87
4/14/2005	6:00	4.0	13.3	1102	3647	373	19.6	5.9	89
4/14/2005	7:00	3.8	14.8	1052	4102	371	19.3	5.9	85
4/14/2005	8:00	3.9	15.5	1001	4036	396	19.4	6.3	82
4/14/2005	9:00	5.2	15.9	1349	4108	396	20.3	7.2	79
4/14/2005	10:00	5.6	19.7	1352	4783	423	20.3	8.5	72
4/14/2005	10:30	4.1	27.4	852	5709	493	21.1	10.0	67

^a AU = Animal Unit (500 kg)

^b Concentration measured at 91cm fan outlet

^c Measured at 91 cm fan outlet

^d Measured at 2m height above surface

^e RH = Relative Humidity in ambient air

Appendix 3. Experimental hourly averaged barn emission rates and meteorological parameters for Summer 2005.

Date	Time	H ₂ S Emission Rate ^a g day ⁻¹ AU ⁻¹	NH ₃ -N Emission Rate ^a g day ⁻¹ AU ⁻¹	H ₂ S conc ^b µg m ⁻³	NH ₃ -N conc ^b µg m ⁻³	Total Fan Flow Rate m ³ min ⁻¹	Barn Temp ^c °C	Ambient Temp ^d °C	RH ^e %
6/19/2005	22:00	0.6	20.8	63	2018	487	25.5	21.0	67
6/19/2005	23:00	0.6	21.3	58	2062	488	25.2	20.5	71
6/19/2005	0:00	0.5	21.1	51	2039	489	24.6	19.6	77
6/20/2005	1:00	0.5	21.9	49	2109	490	24.3	19.3	78
6/20/2005	2:00	0.5	22.2	45	2128	491	24.0	19.0	80
6/20/2005	3:00	0.4	20.9	43	2004	491	23.7	18.8	81
6/20/2005	4:00	0.4	19.4	43	1862	491	23.4	18.2	83
6/20/2005	5:00	0.5	19.7	52	1892	490	23.4	18.0	84
6/20/2005	6:00	0.7	21.9	70	2109	491	23.4	17.7	84
6/20/2005	7:00	0.8	20.7	77	1989	491	24.0	18.6	79
6/20/2005	8:00	0.9	21.9	90	2104	490	25.0	19.6	74
6/20/2005	9:00	0.9	27.0	61	1909	667	25.2	20.6	67
6/20/2005	10:00	0.9	27.8	44	1399	961	25.1	21.3	64
6/20/2005	11:00	0.6	35.9	27	1535	1103	25.1	21.8	61
6/20/2005	12:00	1.2	28.5	53	1233	1090	26.3	22.8	58
6/20/2005	13:00	1.2	29.3	53	1267	1089	25.9	22.8	58
6/20/2005	14:00	1.3	30.3	56	1313	1089	26.7	23.1	57
6/20/2005	15:00	1.5	30.6	64	1329	1087	19.6	23.5	56
6/20/2005	16:00	1.7	31.0	72	1347	1086		23.7	53
6/20/2005	17:00	1.8	32.0	76	1386	1088		22.9	58
6/20/2005	18:00	1.4	29.0	61	1256	1090		22.7	58
6/20/2005	19:00	0.9	22.6	80	2045	533		21.2	62
6/20/2005	20:00	0.8	24.0	76	2299	493		19.8	68
6/20/2005	21:00	0.7	20.9	73	2105	468		17.9	79
6/20/2005	22:00	0.7	18.1	88	2098	406		16.8	82
6/20/2005	23:00	0.7	11.3	137	2128	250		15.5	90
6/20/2005	0:00	0.7	11.6	129	2185	250		14.6	93
6/21/2005	1:00	0.6	11.3	105	2124	250		13.9	95
6/21/2005	2:00	0.5	11.9	95	2245	250		13.4	96
6/21/2005	3:00	0.5	11.9	86	2254	249		13.0	96
6/21/2005	4:00	0.5	11.8	100	2241	249		12.9	96
6/21/2005	5:00	0.6	11.8	112	2241	249		12.4	96
6/21/2005	6:00	0.7	12.7	134	2401	249		12.8	97
6/21/2005	7:00	0.7	22.8	92	2790	379		16.0	89
6/21/2005	8:00	0.7	29.8	71	2857	491		18.6	74
6/21/2005	9:00	1.3	36.4	86	2476	697		20.6	64
6/21/2005	10:00	1.1	44.1	46	1890	1100		21.8	57
6/21/2005	11:00								
6/21/2005	12:00			41	1510		27.7		46
6/21/2005	13:00	1.2	60.6	33	2575	1682	28.3	26.7	42
6/21/2005	14:00	1.6	40.9	35	914	2131	28.9	27.2	41
6/21/2005	15:00	1.9	42.2	41	900	2211	29.3	28.1	40

Appendix 3 (cont). Experimental hourly averaged barn emission rates and meteorological parameters for Summer 2005.

6/21/2005	16:00	2.3	46.6	49	1002	2191	29.3	28.5	40
6/21/2005	17:00	2.7	74.9	58	1616	2184	28.9	28.6	42
6/21/2005	18:00	2.4	33.8	52	729	2185	28.3	28.1	45
6/21/2005	19:00	1.4	21.0	46	694	1447	26.8	26.2	54
6/21/2005	20:00	1.4	23.5	65	1084	1055	25.4	23.3	72
6/21/2005	21:00	1.0	22.6	66	1424	754	25.4	22.1	76
6/21/2005	22:00	0.8	20.2	71	1828	521	25.6	21.3	80
6/21/2005	23:00	0.8	22.1	74	2053	507	25.2	20.5	83
6/21/2005	0:00	0.7	22.0	68	2108	492	24.8	19.9	85
6/22/2005	1:00	0.7	22.2	67	2124	493	24.5	19.6	86
6/22/2005	2:00	0.6	20.6	62	1968	493	24.1	19.4	88
6/22/2005	3:00	0.7	19.7	63	1886	493	23.9	19.0	88
6/22/2005	4:00	0.7	19.5	65	1859	493	23.7	18.7	89
6/22/2005	5:00	0.8	21.2	75	2025	494	23.8	18.7	91
6/22/2005	6:00	1.0	23.4	95	2240	493	24.2	18.9	91
6/22/2005	7:00	1.1	26.4	102	2438	511	24.9	20.3	86
6/22/2005	8:00	1.2	38.5	52	1661	1094	25.1	23.0	76
6/22/2005	9:00	1.3	28.4	56	1227	1092	27.0	25.2	68
6/22/2005	10:00	0.7	22.2	32	968	1082	28.0	26.8	63
6/22/2005	11:00			32	2400		30.1		
6/22/2005	12:00	1.3	35.0	27	886	2183	30.6	30.2	48
6/22/2005	13:00	1.6	33.2	34	717	2184	25.1	31.0	43
6/22/2005	14:00	1.6	33.6	35	727	2177		31.5	40
6/22/2005	15:00	1.7	30.8	37	671	2165		31.9	39
6/22/2005	16:00	2.0	30.0	43	658	2150		32.1	37
6/22/2005	17:00	2.1	35.8	47	779	2167		31.6	39
6/22/2005	18:00	2.0	45.5	43	985	2179		29.1	51
6/22/2005	19:00	1.5	28.0	38	717	1841		27.9	60
6/22/2005	20:00	1.2	28.8	35	867	1548		26.0	69
6/22/2005	21:00	1.4	18.0	61	757	1124		24.5	74
6/22/2005	22:00	1.4	20.6	61	886	1094		23.0	79
6/22/2005	23:00	1.4	21.8	63	954	1080		24.2	73
6/22/2005	0:00	0.9	20.5	40	917	1049		23.3	81
6/23/2005	1:00	0.2	15.0	20	1111	646		21.5	92
6/23/2005	2:00	0.5	14.8	48	1350	518		20.9	95
6/23/2005	3:00	0.6	17.3	48	1523	537		20.3	95
6/23/2005	4:00	0.5	19.1	41	1640	550		19.4	96
6/23/2005	5:00	0.8	20.9	64	1783	553		19.2	96
6/23/2005	6:00	0.9	22.3	74	1918	547		19.3	95
6/23/2005	7:00	1.2	26.8	78	1668	779		20.9	89
6/23/2005	8:00	1.5	26.7	67	1170	1074		23.2	79
6/23/2005	9:00	1.4	27.2	62	1176	1089		25.6	68
6/23/2005	10:00	0.9	30.9	36	1114	1264		27.0	61
6/23/2005	11:00	1.8	60.6	40	1398	2061	26.4	28.1	56
6/23/2005	12:00	2.3	28.5	48	599	2240	29.8	28.8	53
6/23/2005	13:00	1.8	30.4	39	649	2210	30.3	29.1	50
6/23/2005	14:00	2.5	26.5	53	570	2193	31.1	30.2	45
6/23/2005	15:00	2.8	26.1	60	565	2180	31.2	30.5	43

Appendix 3 (cont). Experimental hourly averaged barn emission rates and meteorological parameters for Summer 2005.

6/23/2005	16:00	2.8	26.5	62	573	2180	30.6	30.0	46
6/23/2005	17:00	3.5	22.6	75	492	2168	29.8	29.4	50
6/23/2005	18:00	3.4	20.8	73	450	2176	28.9	28.4	56
6/23/2005	19:00	2.9	18.9	62	406	2195	27.7	27.0	61
6/23/2005	20:00	1.9	12.8	55	369	1639	26.3	25.1	66
6/23/2005	21:00	2.1	12.7	92	548	1092	25.8	23.6	72
6/23/2005	22:00	1.8	12.5	93	698	880	25.0	21.9	81
6/23/2005	23:00	0.9	12.1	88	1159	493	25.2	20.4	88
6/23/2005	0:00	0.8	13.0	74	1240	493	24.8	20.1	87
6/24/2005	1:00	0.7	14.0	70	1339	494	24.1	19.1	92
6/24/2005	2:00	0.7	14.4	67	1377	494	23.7	18.3	95
6/24/2005	3:00	0.8	16.2	77	1543	495	23.3	17.8	95
6/24/2005	4:00	0.8	13.9	73	1320	495	23.0	17.5	95
6/24/2005	5:00	0.9	13.3	83	1265	494	23.0	17.3	96
6/24/2005	6:00	1.0	14.5	97	1386	493	23.6	17.7	97
6/24/2005	7:00	1.0	14.9	95	1432	492	24.7	19.2	97
6/24/2005	8:00	1.4	19.9	86	1258	764	25.1	20.5	97
6/24/2005	8:45	1.8	22.9	74	969	1113	25.1	21.9	93

^a AU = Animal Unit (500 kg)

^b Concentration measured at 91cm fan outlet

^c Measured at 91 cm fan outlet

^d Measured at 2m height above surface

^e RH = Relative Humidity in ambient air

Appendix 4. Experimental hourly averaged barn emission rates and meteorological parameters for Fall 2005.

Date	Time	H ₂ S Emission Rate ^a g day ⁻¹ AU ⁻¹	NH ₃ -N Emission Rate ^a g day ⁻¹ AU ⁻¹	H ₂ S conc ^b μg m ⁻³	NH ₃ -N conc ^b μg m ⁻³	Total Fan Flow Rate m ³ min ⁻¹	Barn Temp ^c °C	Ambient Temp ^d °C	RH ^e %
10/26/2005	15:00	2.2		214		486	23.8	17.0	40
10/26/2005	16:00	2.3		220		485	23.8	17.8	39
10/26/2005	17:00	2.2		262		415	22.6	15.1	58
10/26/2005	18:00	2.2		420		245	20.7	12.2	76
10/26/2005	19:00	2.2		428		246	19.1	9.9	87
10/26/2005	20:00	2.0		451		214	18.6	8.6	90
10/26/2005	21:00	1.8		444		186	18.3	7.6	91
10/26/2005	22:00	1.6		413		183	17.7	7.0	93
10/26/2005	23:00	1.5		390		179	18.0	7.0	93
10/26/2005	0:00	1.3		365		168	17.7	6.8	92
10/27/2005	1:00	1.2		375		157	17.2	6.1	92
10/27/2005	2:00	1.2		369		155	16.9	5.7	94
10/27/2005	3:00	1.1		363		139	16.6	5.3	94
10/27/2005	4:00	1.2		381		146	16.7	5.1	94
10/27/2005	5:00	1.0		343		133	16.5	4.9	94
10/27/2005	6:00	1.1		363		144	16.7	4.4	94
10/27/2005	7:00	1.4		392		173	17.2	3.8	94
10/27/2005	8:00	1.7		395		197	18.0	5.9	91
10/27/2005	9:00	1.8		349		247	18.8	8.9	75
10/27/2005	10:00	2.0		328		286	20.5	11.8	63
10/27/2005	11:00	1.9		248		408	22.1	14.2	52
10/27/2005	12:00					486	23.0	15.6	45
10/27/2005	13:00					485	24.0	16.7	41
10/27/2005	14:00					485		17.1	35
10/27/2005	15:00					485	24.0	17.4	35
10/27/2005	16:00	1.2	30.1	120	2932	484	23.6	17.6	34
10/27/2005	17:00	1.7	22.2	207	2511	416	22.8	16.4	44
10/27/2005	18:00	2.3	14.3	424	2532	265	20.6	11.8	70
10/27/2005	19:00	2.2	12.8	431	2466	245	18.7	9.3	85
10/27/2005	20:00	2.1	9.9	465	2219	211	18.4	8.1	91
10/27/2005	21:00	1.8	9.4	434	2225	200	17.9	7.5	91
10/27/2005	22:00	1.9	9.8	445	2266	204	18.4	7.7	91
10/27/2005	23:00	2.1	11.2	452	2445	215	18.7	9.2	77
10/27/2005	0:00	2.2	12.6	427	2426	245	18.5	9.2	78
10/28/2005	1:00	2.2	12.4	417	2376	245	18.4	9.3	81
10/28/2005	2:00	2.1	11.9	429	2381	235	18.4	9.5	81
10/28/2005	3:00	1.9	11.3	406	2394	222	18.2	8.8	90
10/28/2005	4:00	2.0	11.3	421	2363	225	18.6	9.0	92
10/28/2005	5:00	1.9	11.6	407	2428	224	18.8	9.0	93
10/28/2005	6:00	2.0	11.3	420	2385	223	18.7	8.7	93
10/28/2005	7:00	2.2	12.7	417	2417	247	19.2	8.5	94
10/28/2005	8:00	2.1	12.9	397	2457	248	18.9	8.4	93
10/28/2005	9:00	2.2	12.8	419	2450	247	19.5	8.6	93
10/28/2005	10:00	2.1	14.0	404	2688	246	19.8	9.6	90

Appendix 4 (cont). Experimental hourly averaged barn emission rates and meteorological parameters for Fall 2005.

10/28/2005	11:00	2.0	15.3	355	2647	271	20.7	10.9	81
10/28/2005	12:00	1.9	13.9	367	2749	275	21.4	11.9	67
10/28/2005	13:00					378	22.4	13.3	57
10/28/2005	14:00					451	22.5	13.8	53
10/28/2005	15:00					366	22.2	13.6	55
10/28/2005	16:00	2.2	17.5	342	2712	316	22.1	13.5	54
10/28/2005	17:00	2.2	14.7	387	2544	273	21.3	12.7	59
10/28/2005	18:00	2.4	12.9	459	2510	243	20.2	11.4	66
10/28/2005	19:00	2.4	12.2	458	2370	243	19.0	10.1	73
10/28/2005	20:00	2.1	10.5	473	2302	215	18.7	8.7	85
10/28/2005	21:00	1.9	8.6	486	2153	189	18.3	7.8	89
10/28/2005	22:00	1.9	8.1	490	2139	179	18.2	7.0	90
10/28/2005	23:00	1.8	7.7	497	2121	171	17.6	6.4	92
10/28/2005	0:00	1.7	7.3	462	2030	169	17.6	5.8	93
10/29/2005	1:00	1.6	6.5	488	1981	154	17.0	5.0	93
10/29/2005	2:00	1.4	6.7	456	2103	150	16.8	4.6	94
10/29/2005	3:00	1.5	7.0	464	2141	154	16.5	4.3	94
10/29/2005	4:00	1.3	6.0	427	2055	138	16.2	3.8	94
10/29/2005	5:00	1.2	5.8	405	1973	138	15.6	3.7	94
10/29/2005	6:00	1.5	6.3	456	1992	150	16.0	3.2	94
10/29/2005	7:00	1.7	7.2	474	2005	169	16.2	2.7	95
10/29/2005	8:00	2.0	9.5	487	2324	191	17.7	4.7	91
10/29/2005	9:00	2.2	12.4	443	2449	238	18.1	8.0	75
10/29/2005	10:00	2.3	13.5	437	2581	246	20.1	10.6	63
10/29/2005	11:00	2.2	16.3	393	2836	270	20.5	12.0	51
10/29/2005	12:00	2.3	28.1	276	3256	406	21.8	12.9	46
10/29/2005	13:00	2.3	29.3	253	3223	428	22.3	13.6	43
10/29/2005	14:00	2.2	26.8	236	2852	442	22.4	14.0	41
10/29/2005	15:00	2.3	26.7	231	2667	471	22.4	14.4	39
10/29/2005	16:00	2.4	20.6	309	2601	374	22.7	15.0	37
10/29/2005	17:00	2.4	17.1	401	2823	288	22.3	14.0	42
10/29/2005	18:00	2.6	14.1	506	2718	245	19.6	10.3	66
10/29/2005	19:00	2.3	11.1	520	2471	211	18.0	7.9	80
10/29/2005	20:00	2.2	8.4	575	2146	184	17.6	6.5	87
10/29/2005	21:00	2.0	7.1	580	2067	163	17.4	5.3	91
10/29/2005	22:00	1.7	6.3	549	2040	146	16.7	4.2	93
10/29/2005	23:00	1.7	6.2	543	1963	149	16.4	3.6	94
10/29/2005	0:00	1.6	5.7	524	1920	141	15.7	3.2	94
10/30/2005	1:00	0.9	5.7	212	2105	128	15.6	2.9	95
10/30/2005	2:00	1.5	6.1	537	2144	134	15.5	2.5	95
10/30/2005	3:00	1.3	5.3	512	2041	122	15.3	2.3	95
10/30/2005	4:00	1.3	5.0	525	2065	114	14.8	1.9	96
10/30/2005	5:00	1.3	5.3	486	1977	126	14.5	1.5	96
10/30/2005	6:00	1.3	5.4	478	2016	126	14.5	1.2	96
10/30/2005	7:00	1.5	6.0	512	2088	135	15.2	1.2	96
10/30/2005	8:00	1.6	9.0	438	2374	176	17.0	3.6	96
10/30/2005	9:00	1.5	14.6	294	2781	248	18.5	8.9	82
10/30/2005	10:00	2.6	17.4	423	2820	290	20.2	12.0	56
10/30/2005	11:00	2.7	27.3	323	3202	401	22.0	15.4	42

Appendix 4 (cont). Experimental hourly averaged barn emission rates and meteorological parameters for Fall 2005.

10/30/2005	12:00	2.6	34.5	250	3335	487	23.4	17.6	31
10/30/2005	13:00	2.6	34.5	257	3369	483	24.8	18.9	24
10/30/2005	14:00	2.7	30.2	261	2959	481	25.5	19.9	20
10/30/2005	15:00	2.9	38.0	288	3718	482	25.6	20.7	20
10/30/2005	16:00	3.0	25.2	295	2463	483	25.3	21.4	22
10/30/2005	17:00	3.2	24.2	311	2359	485	24.2	19.7	34
10/30/2005	18:00	3.4	16.9	506	2467	327	21.6	13.5	68
10/30/2005	19:00	3.3	13.1	626	2510	246	19.4	10.0	84
10/30/2005	20:00	2.9	10.7	627	2333	217	18.6	8.2	89
10/30/2005	21:00	2.7	9.0	654	2195	194	18.0	7.1	92
10/30/2005	22:00	2.3	7.9	660	2239	167	17.6	6.2	93
10/30/2005	23:00	2.2	7.2	645	2141	159	17.2	5.4	94
10/30/2005	0:00	2.3	7.0	699	2107	157	17.2	4.7	94
10/31/2005	1:00	1.8	7.2	577	2248	150	16.4	4.2	94
10/31/2005	2:00	1.5	6.2	525	2198	134	16.1	3.7	95
10/31/2005	3:00	1.5	6.0	539	2118	133	15.9	3.1	95
10/31/2005	4:00	1.2	6.1	429	2228	129	15.3	2.5	95
10/31/2005	5:00	1.4	5.8	563	2294	119	15.0	2.0	95
10/31/2005	6:00	0.3	5.7	127	2200	121	14.8	1.7	96
10/31/2005	7:00	1.6	7.4	490	2241	155	16.0	1.4	96
10/31/2005	8:00	2.2	11.0	566	2803	185	17.3	4.3	95
10/31/2005	9:00	2.8	14.9	558	2961	236	19.2	10.3	79
10/31/2005	10:00	3.2	25.9	406	3307	369	21.8	15.4	56
10/31/2005	11:00	2.8	35.4	121	3511	487	23.7	19.3	42

^a AU = Animal Unit (500 kg)

^b Concentration measured at 91cm fan outlet

^c Measured at 91 cm fan outlet

^d Measured at 2m height above surface

^e RH = Relative Humidity in ambient air

Appendix 5. Experimental hourly averaged lagoon flux measurements, meteorological and lagoon parameters for Fall 2004.

Date	Time	H ₂ S Flux $\mu\text{g m}^2 \text{ min}^{-1}$	NH ₃ -N Flux $\mu\text{g m}^2 \text{ min}^{-1}$	Lagoon Temp ^a Celcius	pH ^a	Air Temp ^b Celcius	RH ^c %	SR ^d W m ⁻²	WS ^e m s ⁻¹
10/26/2004	13:00	2.0		17.6	8.07	18.2	57	518	2.6
10/26/2004	14:00	1.7		18.6	8.09	19.2	53	588	2.6
10/26/2004	15:00	0.5		19.2	8.08	19.6	52	455	2.5
10/26/2004	16:00	0.5		19.3	8.09	20.2	50	335	1.9
10/26/2004	17:00	0.6		19.3	8.09	19.2	57	118	1.3
10/26/2004	18:00	0.4		18.9	8.10	15.7	79	5	0.1
10/26/2004	19:00	0.4		18.4	8.11	12.6	92	0	0.2
10/26/2004	20:00	0.3		18.0	8.11	11.3	94	0	0.1
10/26/2004	21:00	0.3		17.7	8.11	10.4	95	0	0.4
10/26/2004	22:00	0.3		17.4	8.11	9.7	96	0	0.2
10/26/2004	23:00	0.3		17.1	8.11	9.2	95	0	0.4
10/26/2004	0:00	0.3		16.9	8.11	8.4	96	0	0.3
10/27/2004	1:00	0.3		16.7	8.10	7.9	96	0	0.3
10/27/2004	2:00	0.3		16.5	8.10	7.5	96	0	0.2
10/27/2004	3:00	0.4		16.4	8.09	7.0	97	0	0.1
10/27/2004	4:00	0.3		16.3	8.09	6.7	97	0	0.1
10/27/2004	5:00	0.3		16.1	8.09	6.5	97	0	0.1
10/27/2004	6:00	0.3		15.9	8.09	6.2	97	0	0.1
10/27/2004	7:00	0.3		15.8	8.11	6.1	97	10	0.2
10/27/2004	8:00	0.2		15.7	8.10	7.7	96	104	0.7
10/27/2004	9:00	0.2		15.8	8.11	12.6	87	296	1.1
10/27/2004	10:00	0.3		16.0	8.09	16.7	73	430	1.1
10/27/2004	11:00			16.1	8.09	18.9	63	526	1.5
10/27/2004	12:00			16.3	8.09	19.4	59	344	1.7
10/27/2004	13:00			16.4	8.10	20.5	53	567	2.0
10/27/2004	14:00			17.5	8.09	20.0	55	298	2.0
10/27/2004	15:00	0.4	1280	17.6	8.08	19.7	58	185	1.6
10/27/2004	16:00	0.4	1356	18.5	8.09	19.3	62	107	1.5
10/27/2004	17:00	0.4	1556	18.7	8.09	18.7	70	42	1.0
10/27/2004	18:00	0.4	1652	18.8	8.11	17.8	80	3	0.2
10/27/2004	19:00	0.3	1778	19.1	8.10	16.6	86	0	0.2
10/27/2004	20:00	0.3	1829	19.0	8.11	16.1	88	0	0.2
10/27/2004	21:00	0.3	1837	18.9	8.11	16.1	88	0	0.4
10/27/2004	22:00	0.3	1764	18.4	8.07	16.3	83	0	0.3
10/27/2004	23:00	0.3	1665	17.9	8.07	15.9	80	0	0.7
10/27/2004	0:00	0.3	1587	17.5	8.09	15.5	81	0	0.6
10/28/2004	1:00	0.3	1507	17.2	8.11	14.5	83	0	0.7
10/28/2004	2:00	0.3	1449	16.9	8.10	14.1	86	0	0.5
10/28/2004	3:00	0.3	1400	16.8	8.10	13.8	88	0	0.6
10/28/2004	4:00	0.3	1346	16.6	8.11	13.7	89	0	0.9
10/28/2004	5:00	0.2	1298	16.5	8.14	13.6	88	0	1.0
10/28/2004	6:00	0.2	1257	16.4	8.12	13.4	89	0	1.0
10/28/2004	7:00	0.3	1233	16.3	8.11	13.4	89	2	1.0
10/28/2004	8:00	0.3	1212	16.2	8.12	13.6	87	40	1.2

Appendix 5. Experimental hourly averaged lagoon flux measurements, meteorological and lagoon parameters for Fall 2004.

10/28/2004	9:00	0.3	1184	16.3	8.12	14.8	81	175	1.8
10/28/2004	10:00	0.3	1110	16.5	8.11	17.2	67	320	2.1
10/28/2004	11:00	0.3	1141	16.9	8.11	18.3	58	464	2.2
10/28/2004	12:00			18.0	8.09	19.1	55	592	2.2
10/28/2004	13:00			18.6	8.09	20.2	52	628	2.4
10/28/2004	14:00			19.5	8.10	20.1	53	439	2.3
10/28/2004	15:00	0.3		19.8	8.11	19.8	53	237	1.9
10/28/2004	16:00	0.4		19.7	8.09	19.3	54	107	1.4
10/28/2004	17:00	0.3		20.0	8.12	18.7	65	32	0.6
10/28/2004	18:00	0.3		20.1	8.12	17.8	72	1	0.4
10/28/2004	19:00	0.3		19.7	8.11	17.3	70	0	0.6
10/28/2004	20:00	0.3		19.5	8.11	16.5	77	0	0.4
10/28/2004	21:00	0.3		19.2	8.11	15.2	81	0	0.6
10/28/2004	22:00	0.3		18.7	8.13	14.9	82	0	1.4
10/28/2004	23:00	0.3		18.2	8.12	14.3	84	0	1.6
10/28/2004	0:00	0.2		17.9	8.13	12.7	92	0	0.8
10/29/2004	1:00	0.2		17.6	8.14	11.8	95	0	0.4
10/29/2004	2:00			17.2	8.13	10.9	97	0	0.4
10/29/2004	3:00			17.0	8.13	10.4	97	0	0.4
10/29/2004	4:00			16.9	8.14	11.2	95	0	0.5
10/29/2004	5:00			16.8	8.12	11.3	96	0	0.6
10/29/2004	6:00	0.2		16.7	8.11	11.6	96	0	0.7
10/29/2004	7:00			16.6	8.12	11.7	96	5	0.8
10/29/2004	8:00	0.2		16.5	8.13	12.3	94	86	0.8
10/29/2004	9:00	0.2		16.8	8.14	14.8	88	167	0.8
10/29/2004	10:00	0.2		17.4	8.12	17.3	82	192	1.1
10/29/2004	11:00	0.1		17.6	8.14	17.4	79	70	1.2
10/29/2004	12:00	0.0		17.6	8.13	17.9	78	162	1.3
10/29/2004	13:00	0.0		18.0	8.15	18.2	76	133	1.4
10/29/2004	14:00	0.1	1495	18.0	8.14	17.9	79	130	2.0
10/29/2004	15:00	0.5	1499	18.1	8.12	18.2	83	78	1.8
10/29/2004	16:00	0.5	1452	17.9	8.12	18.4	83	77	1.8
10/29/2004	17:00	0.4	1458	17.8	8.13	17.9	84	44	1.9
10/29/2004	18:00	0.4	1371	17.5	8.12	18.7	83	1	1.4
10/29/2004	19:00	0.4	1332	17.3	8.14	17.6	86	0	2.1
10/29/2004	20:00	0.4	1286	17.0	8.14	17.5	88	0	1.3
10/29/2004	21:00	0.3	1272	17.0	8.13	16.4	92	0	0.6
10/29/2004	22:00	0.2	1260	17.0	8.10	16.9	92	0	0.6
10/29/2004	23:00	0.3	1235	16.9	8.10	17.8	91	0	1.2
10/29/2004	0:00	0.3	1225	16.9	8.13	17.7	93	0	1.8
10/30/2004	1:00	0.3	1199	16.9	8.10	18.2	91	0	1.6
10/30/2004	2:00	0.2	1186	16.8	8.09	18.7	90	0	1.5
10/30/2004	3:00	0.3	1161	16.8	8.08	18.3	91	0	1.7
10/30/2004	4:00	0.3	1165	16.9	8.08	18.3	92	0	1.6
10/30/2004	5:00	0.3	1139	16.9	8.06	19.4	89	0	1.2
10/30/2004	6:00	0.3	1117	16.9	8.03	19.6	89	0	1.3
10/30/2004	7:00	0.2	1125	16.8	8.07	20.0	88	10	1.3
10/30/2004	8:00	0.1	1144	16.9	8.10	19.8	90	83	1.5
10/30/2004	9:00			17.3	8.10	20.9	85	296	2.5
10/30/2004	10:00	0.6		18.9	8.08	24.0	73	292	2.2

Appendix 5 (cont). Experimental hourly averaged lagoon flux measurements, meteorological and lagoon parameters for Fall 2004.

10/30/2004	11:00	0.3		-1734.8	1755.66	25.2	67	452	2.9
10/30/2004	12:00	0.0		-2318.6	822.74	26.1	66	558	3.0
10/30/2004	13:00	0.0		22.2	150.39	26.4	64	455	4.0
10/30/2004	14:00	0.2		22.4	7.71	26.6	65	432	3.3
10/30/2004	15:00	0.4		22.9	8.05	26.3	66	331	2.9
10/30/2004	16:00	0.2	2398	23.3	8.08	26.0	68	238	2.9
10/30/2004	17:00	0.8	2106	22.9	8.08	25.2	71	83	2.7
10/30/2004	18:00	0.5	1864	22.1	8.07	23.7	78	4	2.4
10/30/2004	19:00	0.4	2071	21.4	8.04	22.5	83	0	1.5
10/30/2004	20:00	0.3	1917	20.8	8.05	22.1	85	0	2.3
10/30/2004	21:00	0.4	1850	20.5	8.07	21.4	88	0	2.5
10/30/2004	22:00	0.3	1709	20.3	8.07	21.2	90	0	2.7
10/30/2004	23:00	0.4	1561	19.8	8.08	21.0	91	0	2.7
10/30/2004	0:00	0.3	1436	19.6	8.09	20.9	91	0	2.8
10/31/2004	1:00	0.3	1390	19.5	8.09	20.9	91	0	2.8
10/31/2004	2:00	0.3	1360	19.3	8.10	20.8	92	0	2.7
10/31/2004	3:00	0.3	1358	19.2	8.10	20.9	92	0	2.7
10/31/2004	4:00	0.2	1378	19.1	8.11	20.9	91	0	2.4
10/31/2004	5:00	0.2	1387	19.0	8.10	21.0	90	0	1.9
10/31/2004	6:00	0.2	1364	18.8	8.09	20.9	90	0	1.4
10/31/2004	7:00	0.2	1334	18.7	8.09	20.9	90	8	1.6
10/31/2004	8:00		1337	18.6	8.09	20.8	90	77	1.8
10/31/2004	9:00	0.2	1381	18.9	8.10	21.9	85	265	2.3
10/31/2004	10:00		1816	20.0	8.12	24.0	74	443	2.6
10/31/2004	11:00		2322	21.5	8.10	26.4	63	560	1.9
10/31/2004	12:00	0.3	2985	22.9	8.08	27.9	53	616	2.1
10/31/2004	13:00		3202	25.0	8.05	29.1	44	625	2.1
10/31/2004	14:00			26.9	8.03	29.4	41	555	2.7
10/31/2004	15:00			26.9	8.04	29.0	43	389	3.2
10/31/2004	16:00		3305	26.5	8.05	29.0	46	283	2.3
10/31/2004	17:00		3138	25.5	8.09	27.7	51	96	1.8
10/31/2004	18:00	0.2	2920	24.3	8.07	25.0	64	4	1.5
10/31/2004	19:00	0.2	2629	23.4	8.09	22.9	73	0	1.2
10/31/2004	20:00	0.2	2381	22.5	8.10	21.9	78	0	1.2
10/31/2004	21:00	0.3	2211	22.0	8.06	21.3	79	0	1.2
10/31/2004	22:00	0.2	2067	21.4	8.06	21.6	78	0	1.3
10/31/2004	23:00	0.2	1922	21.0	8.07	21.1	80	0	1.0
10/31/2004	0:00	0.2	1820	20.6	8.09	21.2	81	0	1.1
11/1/2004	1:00	0.2	1718	20.3	8.09	21.0	83	0	1.2
11/1/2004	2:00	0.2	1627	20.1	8.09	21.0	84	0	1.4
11/1/2004	3:00	0.2	1544	20.0	8.10	20.0	87	0	1.0
11/1/2004	4:00	0.2	1488	19.8	8.08	17.9	94	0	0.3
11/1/2004	5:00	0.2	1438	19.6	8.05	18.9	90	0	0.9
11/1/2004	6:00	0.2	1366	19.5	8.06	18.8	90	0	0.8
11/1/2004	7:00	0.2	1373	19.5	8.04	17.4	95	8	0.3
11/1/2004	8:00	0.2	1458	19.4	8.05	18.5	92	92	0.4
11/1/2004	9:00	0.2	1585	19.4	8.04	22.2	83	260	1.2
11/1/2004	10:00	0.2	1927	19.5	8.03	24.3	72	398	1.0
10/27/2004	11:00	0.3	1997	19.6	8.02	26.0	58	486	1.2

Appendix 5 (cont). Experimental hourly averaged lagoon flux measurements, meteorological and lagoon parameters for Fall 2004.

^a Measured at depth of ~6-7cm

^b Measured at 2m height above surface

^c RH = Relative Humidity

^d SR = Solar Radiation

^e WS = Wind Speed measured at 10m height above surface

Appendix 6. Experimental hourly averaged lagoon flux measurements, meteorological and lagoon parameters for Winter 2005.

Date	Time	H ₂ S Flux	NH ₃ -N Flux	Lagoon Temp ^a	pH ^a	Air Temp ^b	RH ^c	SR ^d	WS ^e
		µg m ² min ⁻¹	µg m ² min ⁻¹	Celcius		Celcius	%	W m ⁻²	m s ⁻¹
2/15/2005	16:00	0.1	1491	13.5	8.02	18.6	49	111	0.9
2/15/2005	17:00	0.1	1604	13.9	8.02	19.7	47	203	0.6
2/15/2005	18:00	0.1	1872	13.9	8.04	17.3	58	30	0.9
2/15/2005	19:00	0.1	1676	14.5	8.10	14.9	68	0	2.0
2/15/2005	20:00	0.2	1484	13.2	8.11	13.5	69	0	2.1
2/15/2005	21:00	0.3	1410	12.5	8.09	12.2	76	0	1.7
2/15/2005	22:00	0.2	1445	12.7	8.11	11.9	77	0	2.0
2/15/2005	23:00	0.2	1472	12.5	8.12	11.2	82	0	1.4
2/15/2005	0:00	0.2	1480	12.3	8.12	11.0	83	0	1.5
2/16/2005	1:00	0.1	1484	12.2	8.15	10.3	86	0	1.4
2/16/2005	2:00	0.1	1491	12.0	8.13	9.8	89	0	0.9
2/16/2005	3:00	0.1	1498	12.0	8.15	9.5	91	0	0.8
2/16/2005	4:00	0.1	1486	11.8	8.13	8.6	93	0	1.0
2/16/2005	5:00	0.0	1461	11.6	8.19	9.1	95	0	1.9
2/16/2005	6:00	0.2	1420	11.2	8.15	9.9	96	0	1.8
2/16/2005	7:00	0.2	1377	11.0	8.15	9.5	97	0	1.5
2/16/2005	8:00	0.1	1385	10.7	8.12	9.7	98	37	2.1
2/16/2005	9:00			10.8	8.14	11.1	98	139	2.5
2/16/2005	10:00			11.4	8.11	12.8	92	154	3.1
2/16/2005	11:00			11.6	8.12	13.4	91	171	3.4
2/16/2005	12:00			11.8	8.12	14.1	89	173	3.6
2/16/2005	13:00			12.1	8.10	15.7	81	269	3.3
2/16/2005	14:00	0.1	984	13.1	8.08	18.5	69	574	4.1
2/16/2005	15:00	0.2	951	13.7	8.07	19.5	64	421	3.8
2/16/2005	16:00	0.1	1102	13.9	8.06	20.1	63	359	2.7
2/16/2005	17:00	0.1	1370	14.3	8.07	19.6	65	105	2.1
2/16/2005	18:00	0.1	1374	14.1	8.09	19.0	67	52	2.9
2/16/2005	19:00	0.0	1350	13.6	8.09	17.3	75	0	2.1
2/16/2005	20:00	0.0	1525	13.8	8.10	16.8	80	0	1.1
2/16/2005	21:00	0.0	1675	14.2	8.09	15.9	83	0	1.2
2/16/2005	22:00	0.2	1416	13.3	8.07	14.2	76	0	2.8
2/16/2005	23:00	0.0	1502	13.1	8.09	11.6	91	0	1.2
2/16/2005	0:00	-0.1	1500	13.4	8.12	11.4	90	0	1.4
2/17/2005	1:00	0.1	1314	12.6	8.09	10.3	86	0	3.2
2/17/2005	2:00	0.0	1350	12.3	8.08	9.0	92	0	1.7
2/17/2005	3:00	0.0	1366	12.6	8.11	8.6	90	0	2.0
2/17/2005	4:00	-0.1	1302	12.3	8.09	7.9	81	0	2.0
2/17/2005	5:00	-0.1	1288	12.1	8.12	7.0	85	0	1.0
2/17/2005	6:00	-0.1	1259	12.0	8.15	7.0	79	0	1.4
2/17/2005	7:00	-0.1	1221	11.8	8.11	6.5	68	1	1.7
2/17/2005	8:00	0.0	1204	11.7	8.10	5.9	75	40	0.8
2/17/2005	9:00			11.6	8.13	6.9	67	164	1.6
2/17/2005	10:00			11.7	8.11	7.8	57	246	2.0
2/17/2005	11:00			12.0	8.10	8.7	52	374	2.1

Appendix 6 (cont). Experimental hourly averaged lagoon flux measurements, meteorological and lagoon parameters for Winter 2005.

2/17/2005	12:00			12.3	8.10	10.3	46	641	1.9
2/17/2005	13:00	0.1		12.6	8.09	11.3	46	562	2.2
2/17/2005	14:00	0.1		13.4	8.08	12.2	45	650	2.6
2/17/2005	15:00	0.1		13.8	8.09	13.2	39	534	2.9
2/17/2005	16:00	0.0		13.9	8.10	13.8	32	478	3.2
2/17/2005	17:00	0.0		13.1	8.10	12.8	32	282	3.0
2/17/2005	18:00	0.0		13.2	8.13	10.8	38	63	2.3
2/17/2005	19:00	0.0		13.8	8.18	8.3	50	0	1.0
2/17/2005	20:00	-0.1		13.5	8.17	6.7	65	0	0.5
2/17/2005	21:00	0.0		13.1	8.16	6.1	54	0	1.7
2/17/2005	22:00	-0.1		12.5	8.14	6.2	47	0	1.8
2/17/2005	23:00	0.0		12.2	8.10	5.1	47	0	1.5
2/17/2005	0:00	0.0		11.9	8.09	3.7	59	0	0.7
2/18/2005	1:00	-0.1		11.8	8.09	3.0	74	0	0.3
2/18/2005	2:00	-0.1		11.6	8.10	0.9	81	0	0.5
2/18/2005	3:00	-0.1		11.4	8.09	-1.0	90	0	0.7
2/18/2005	4:00	-0.1		11.2	8.08	-1.5	92	0	0.3
2/18/2005	5:00	-0.1		11.0	8.08	-1.9	93	0	1.4
2/18/2005	6:00	-0.1		10.8	8.09	-0.9	86	0	0.8
2/18/2005	7:00	0.0		10.7	8.09	-1.4	89	1	0.6
2/18/2005	8:00	-0.1		10.5	8.09	-1.4	83	67	0.7
2/18/2005	9:00	-0.1		10.4	8.09	3.7	53	276	2.1
2/18/2005	10:00			10.5	8.09	5.5	40	446	3.4
2/18/2005	11:00			10.7	8.10	7.0	35	615	3.6
2/18/2005	12:00			10.9	8.10	7.5	31	716	3.9
2/18/2005	13:00			11.3	8.10	8.1	28	761	3.8
2/18/2005	14:00	0.1	1453	11.6	8.11	7.9	25	720	4.1
2/18/2005	15:00	0.0	1307	12.2	8.12	8.2	27	640	3.6
2/18/2005	16:00	0.1	1227	12.2	8.10	8.1	25	467	3.6
2/18/2005	17:00	-0.1	1262	12.2	8.11	8.2	26	284	2.7
2/18/2005	18:00	-0.1	1170	12.0	8.11	6.6	34	66	1.8
2/18/2005	19:00	-0.1	1056	11.7	8.13	3.3	53	0	0.4
2/18/2005	20:00	-0.1	1010	11.5	8.11	2.3	63	0	0.6
2/18/2005	21:00	-0.1	944	11.4	8.11	-0.4	80	0	0.2
2/18/2005	22:00	-0.1	914	11.3	8.10	-0.9	81	0	0.2
2/18/2005	23:00	-0.1	904	11.1	8.09	-1.6	87	0	0.5
2/18/2005	0:00	-0.1	909	10.8	8.10	-2.4	92	0	0.7
2/19/2005	1:00	-0.1	891	10.6	8.10	-2.5	94	0	0.2
2/19/2005	2:00	-0.1	895	10.4	8.11	-3.1	95	0	0.5
2/19/2005	3:00	-0.1	900	10.3	8.11	-3.4	97	0	0.5
2/19/2005	4:00	-0.1	895	10.1	8.11	-3.7	96	0	0.5
2/19/2005	5:00	-0.1	880	10.0	8.12	-4.6	95	0	0.5
2/19/2005	6:00	-0.1	871	9.8	8.13	-4.6	97	0	0.3
2/19/2005	7:00	-0.1	867	9.7	8.11	-5.0	97	2	0.4
2/19/2005	8:00	-0.1	886	9.5	8.11	-4.4	96	44	0.3
2/19/2005	9:00	-0.1	966	9.5	8.10	0.6	70	202	0.4
2/19/2005	10:00	0.0	1045	9.5	8.11	4.4	54	444	0.8
2/19/2005	11:00	-0.1	1280	10.0	8.12	6.7	39	613	1.3
2/19/2005	12:00			10.0	8.12	8.2	34	708	1.5
2/19/2005	13:00			10.2	8.12	9.8	32	758	2.0

Appendix 6 (cont). Experimental hourly averaged lagoon flux measurements, meteorological and lagoon parameters for Winter 2005.

2/19/2005	14:00			10.3	8.10	10.8	29	721	2.1
2/19/2005	15:00	0.2	2027	11.0	8.12	11.3	28	637	2.0
2/19/2005	16:00	0.0	1727	10.9	8.12	12.2	27	489	1.8
2/19/2005	17:00	0.0	1900	12.4	8.11	12.5	29	265	1.5
2/19/2005	18:00	-0.2	1813	14.1	8.12	10.6	35	69	1.1
2/19/2005	19:00	-0.2	1554	12.6	8.12	7.5	52	0	0.4
2/19/2005	20:00	-0.1	1529	12.7	8.18	6.3	57	0	1.4
2/19/2005	21:00	-0.1	1540	12.3	8.20	6.6	59	0	1.7
2/19/2005	22:00	-0.1	1458	11.7	8.19	6.2	62	0	1.7
2/19/2005	23:00	-0.1	1354	11.3	8.18	5.7	66	0	1.3
2/19/2005	0:00	-0.1	1250	10.7	8.17	3.9	75	0	0.6
2/20/2005	1:00	0.0	1233	10.3	8.15	3.0	80	0	0.9
2/20/2005	2:00	0.0	1169	9.9	8.16	0.6	90	0	0.3
2/20/2005	3:00	0.1	1155	9.5	8.14	0.0	91	0	0.2
2/20/2005	4:00	0.2	1170	9.3	8.12	0.7	89	0	0.1
2/20/2005	5:00	0.2	1149	9.2	8.13	1.7	88	0	0.4
2/20/2005	6:00	0.2	1159	9.2	8.12	2.6	86	0	1.0
2/20/2005	7:00	0.2	1178	9.2	8.11	4.0	83	1	0.6
2/20/2005	8:00	0.1	1209	9.2	8.11	5.2	80	20	0.4
2/20/2005	9:00	-0.1	1287	9.1	8.16	6.3	75	127	0.8
2/20/2005	10:00	-0.1	1499	9.1	8.15	10.1	66	243	1.2
2/20/2005	11:00	0.0	1135	9.2	8.13	11.3	59	270	1.3
2/20/2005	12:00			9.6	8.09	13.1	52	309	1.6
2/20/2005	13:00			10.8	8.11	14.1	45	330	1.8
2/20/2005	14:00	0.1	1467	11.2	8.13	14.7	43	311	1.8
2/20/2005	15:00	0.0	1485	11.3	8.14	15.2	40	294	2.1
2/20/2005	16:00	0.0	1302	11.0	8.15	14.0	40	98	2.3
2/20/2005	17:00	0.0	1395	10.8	8.14	13.9	43	78	1.0
2/20/2005	18:00	0.0	1472	10.6	8.13	13.6	52	13	0.6
2/20/2005	19:00	0.0	1477	10.9	8.10	12.5	57	0	0.5
2/20/2005	20:00	-0.1	1412	11.0	8.10	11.1	65	0	0.7
2/20/2005	21:00	0.0	1358	11.1	8.11	10.1	74	0	0.3
2/20/2005	22:00	0.0	1327	11.0	8.13	9.5	87	0	0.6
2/20/2005	23:00	0.0	1298	10.8	8.14	9.8	84	0	1.5
2/20/2005	0:00	0.1	1244	10.5	8.15	9.6	84	0	1.8
2/21/2005	1:00	0.1	1209	10.2	8.16	8.8	89	0	1.4
2/21/2005	2:00	0.0	1184	10.1	8.16	8.5	92	0	1.5
2/21/2005	3:00	0.0	1171	10.0	8.16	9.3	84	0	2.4
2/21/2005	4:00	0.0	1162	9.9	8.15	9.4	85	0	2.1
2/21/2005	5:00	0.1	1120	9.8	8.14	9.9	88	0	2.5
2/21/2005	6:00	0.1	1117	9.8	8.12	11.7	89	0	2.4
2/21/2005	7:00	1.2	1030	9.8	8.13	13.5	87	1	3.9
2/21/2005	8:00	0.6	1059	9.8	8.13	13.7	86	64	3.6
2/21/2005	9:00	0.2	1125	10.1	8.13	14.9	82	146	3.2
2/21/2005	10:00	0.3	1104	10.3	8.13	15.6	79	115	4.1
2/21/2005	11:00	0.6	1118	10.6	8.13	16.7	74	245	4.9

^a Measured at depth of ~6-7cm

^b Measured at 2m height above surface

^c RH = Relative Humidity

Appendix 6 (cont). Experimental hourly averaged lagoon flux measurements, meteorological and lagoon parameters for Winter 2005.

^d SR = Solar Radiation

^e WS = Wind Speed measured at 10m height above surface

Appendix 7. Experimental hourly averaged lagoon flux measurements, meteorological and lagoon parameters for Spring 2005.

Date	Time	H ₂ S Flux μg m ² min ⁻¹	NH ₃ -N Flux μg m ² min ⁻¹	Lagoon Temp ^a Celcius	pH ^a	Air Temp ^b Celcius	RH ^c %	SR ^d W m ⁻²	WS ^e m s ⁻¹
4/14/2005	12:00	40.4	927	14.3	8.07	11.5	57	304	4.2
4/14/2005	13:00	117.4	888	14.2	8.08	12.8	48	387	4.7
4/14/2005	14:00	71.4	1035	14.2	8.09	14.5	40	400	4.6
4/14/2005	15:00	8.1	1074	14.2	8.09	15.4	34	401	5.1
4/14/2005	16:00	69.2	1270	14.6	8.09	15.7	33	428	4.7
4/14/2005	17:00	6.1	1506	14.6	8.10	14.9	38	190	3.5
4/14/2005	18:00	23.3	1294	14.6	8.10	14.3	38	79	3.6
4/14/2005	19:00	4.3	1391	14.5	8.11	13.0	45	11	2.7
4/14/2005	20:00	3.8	1362	14.3	8.11	11.9	48	0	2.7
4/14/2005	21:00	5.1	1159	14.2	8.11	10.6	57	0	2.0
4/14/2005	22:00	2.8	1205	14.0	8.11	9.7	63	0	2.3
4/14/2005	23:00	2.5	1054	14.0	8.11	9.4	61	0	4.0
4/14/2005	0:00	2.3	1010	14.0	8.10	8.3	60	0	3.7
4/15/2005	1:00	1.8	1005	13.7	8.10	7.3	65	0	2.9
4/15/2005	2:00	2.2	886	13.4	8.09	6.8	67	0	3.2
4/15/2005	3:00	1.5	887	13.4	8.09	6.6	70	0	3.2
4/15/2005	4:00	1.3	868	13.2	8.09	6.5	74	0	3.3
4/15/2005	5:00	1.4	789	12.9	8.09	6.7	76	0	4.0
4/15/2005	6:00	1.1	808	12.8	8.11	7.0	79	4	4.0
4/15/2005	7:00	1.4	821	12.6	8.10	7.7	74	91	4.3
4/15/2005	8:00	2.4	799	12.4	8.11	8.7	65	269	6.1
4/15/2005	9:00	8.2	887	12.4	8.09	9.0	59	439	7.2
4/15/2005	10:00	4.6	1020	12.7	8.09	10.1	55	660	6.4
4/15/2005	11:00								
4/15/2005	12:00	1.0	2298	14.2	8.10	12.4	43	935	7.6
4/15/2005	13:00	0.6	2534	14.6	8.10	13.0	44	927	5.8
4/15/2005	14:00	0.6	2658	15.2	8.07	13.3	42	889	6.5
4/15/2005	15:00	0.5	2713	15.7	8.09	13.5	42	779	6.0
4/15/2005	16:00	0.5	2703	16.0	8.09	13.4	40	614	6.4
4/15/2005	17:00	0.4	2623	16.0	8.11	12.5	39	413	6.5
4/15/2005	18:00	0.3	2673	16.0	8.10	11.3	40	174	6.1
4/15/2005	19:00	0.3	2559	15.8	8.10	9.8	46	24	5.7
4/15/2005	20:00	0.2	2502	15.5	8.12	8.3	47	0	5.3
4/15/2005	21:00	0.3	2404	15.1	8.08	7.3	47	0	5.0
4/15/2005	22:00	0.3	2233	14.7	8.07	6.6	48	0	4.7
4/15/2005	23:00	0.2	2261	14.4	8.08	5.8	52	0	3.8
4/15/2005	0:00	0.2	2179	14.1	8.11	5.4	52	0	3.6
4/16/2005	1:00	0.2	2040	13.8	8.11	5.3	53	0	3.5
4/16/2005	2:00	0.2	1999	13.7	8.10	5.2	56	0	3.6
4/16/2005	3:00	0.1	1972	13.5	8.11	4.6	59	0	3.1
4/16/2005	4:00	0.2	1932	13.3	8.14	3.8	62	0	2.3
4/16/2005	5:00	0.1	1769	13.0	8.12	3.5	65	0	2.9
4/16/2005	6:00	0.1	1794	12.9	8.12	3.4	68	5	2.8

Appendix 7 (cont). Experimental hourly averaged lagoon flux measurements, meteorological and lagoon parameters for Spring 2005.

4/16/2005	7:00	0.1	1747	12.7	8.12	4.0	67	82	3.2
4/16/2005	8:00	0.2	1771	12.4	8.12	5.5	65	206	3.6
4/16/2005	9:00	0.1	2047	12.6	8.12	7.6	65	374	4.4
4/16/2005	10:00	0.2	2187	12.6	8.11	9.0	65	372	4.4
4/16/2005	11:00	0.3	2672	13.2	8.08	11.3	59	811	5.0
4/16/2005	12:00	0.3	2720	13.6	8.09	13.0	54	842	5.1
4/16/2005	13:00	0.3	2713	14.0	8.09	14.2	48	839	5.2
4/16/2005	14:00	0.3	2828	14.6	8.10	15.1	43	786	5.0
4/16/2005	15:00	0.3	2950	16.0	8.09	15.8	39	751	4.6
4/16/2005	16:00	0.3	2958	16.1	8.12	15.6	37	539	4.9
4/16/2005	17:00	0.2	2953	16.1	8.12	15.0	34	310	4.7
4/16/2005	18:00	0.1	2815	15.8	8.12	14.1	37	128	3.9
4/16/2005	19:00	0.1	2707	15.8	8.11	12.4	42	16	2.9
4/16/2005	20:00	0.1	2611	15.6	8.11	10.8	43	0	2.5
4/16/2005	21:00	0.1	2437	15.5	8.12	10.0	39	0	3.1
4/16/2005	22:00	0.2	2381	15.3	8.13	8.1	56	0	1.7
4/16/2005	23:00	0.1	2235	15.0	8.12	6.8	65	0	1.5
4/16/2005	0:00	0.1	2099	14.8	8.14	5.8	70	0	1.9
4/17/2005	1:00	0.1	1989	14.6	8.13	4.9	73	0	1.9
4/17/2005	2:00	0.1	1855	14.4	8.13	3.6	79	0	1.1
4/17/2005	3:00	0.1	1763	14.0	8.13	2.8	84	0	1.0
4/17/2005	4:00	0.1	1684	13.7	8.13	2.5	86	0	1.0
4/17/2005	5:00	0.1	1633	13.5	8.11	2.1	90	0	0.7
4/17/2005	6:00	0.1	1565	13.3	8.11	1.3	94	7	0.4
4/17/2005	7:00	0.1	1619	13.2	8.12	2.8	92	137	0.7
4/17/2005	8:00	0.1	1802	13.2	8.14	5.8	70	352	2.0
4/17/2005	9:00	0.1	2330	13.5	8.13	9.6	41	557	2.8
4/17/2005	10:00	0.1	2677	13.7	8.12	11.6	30	695	3.1
4/17/2005	11:00								
4/17/2005	12:00	0.1	2884	15.5	8.15	16.5	26	953	2.7
4/17/2005	13:00	0.3	2925	16.1	8.14	17.3	24	943	2.6
4/17/2005	14:00	0.4	2942	16.3	8.13	18.7	22	897	2.3
4/17/2005	15:00	0.4	3054	17.8	8.11	19.6	21	789	1.9
4/17/2005	16:00	0.4	3216	19.8	8.14	20.3	20	624	1.7
4/17/2005	17:00	0.4	3108	18.5	8.11	20.7	19	424	1.3
4/17/2005	18:00	0.3	3123	18.7	8.15	20.3	23	182	0.8
4/17/2005	19:00	0.2	3054	17.9	8.14	16.2	46	19	0.5
4/17/2005	20:00	0.2	2951	17.0	8.13	12.9	58	0	1.7
4/17/2005	21:00	0.2	2685	16.3	8.10	12.2	60	0	1.4
4/17/2005	22:00	0.3	2435	15.9	8.10	9.7	72	0	1.0
4/17/2005	23:00	0.3	2266	15.5	8.12	9.6	73	0	1.4
4/17/2005	0:00	0.2	2163	15.2	8.11	8.5	79	0	0.9
4/18/2005	1:00	0.3	2067	15.1	8.09	7.4	85	0	0.7
4/18/2005	2:00	0.2	1998	15.0	8.07	6.9	90	0	0.9
4/18/2005	3:00	0.2	1944	14.8	8.09	7.0	88	0	1.1
4/18/2005	4:00	0.2	1900	14.6	8.06	6.2	92	0	1.0
4/18/2005	5:00	0.2	1859	14.4	8.03	6.3	92	0	1.1
4/18/2005	6:00	0.2	1893	14.4	8.05	7.4	89	7	1.1

Appendix 7 (cont). Experimental hourly averaged lagoon flux measurements, meteorological and lagoon parameters for Spring 2005.

4/18/2005	7:00	0.2	2003	14.3	8.10	8.3	87	126	1.2
4/18/2005	8:00	0.2	2439	14.6	8.10	12.1	69	333	2.3
4/18/2005	9:00	0.2	2854	15.5	8.08	14.3	57	481	2.7
4/18/2005	10:00	0.3	2988	17.0	8.08	17.4	50	687	2.4
4/18/2005	11:00								
4/18/2005	12:00								
4/18/2005	13:00								
4/18/2005	14:00	0.9	2975	16.8	8.04	25.5	26	850	1.7
4/18/2005	15:00	1.2	3036	17.6	8.08	26.2	25	749	1.9
4/18/2005	16:00	5.1	3118	18.6	8.08	26.4	24	585	1.7
4/18/2005	17:00	7.1	3163	19.1	8.08	26.2	24	368	1.6
4/18/2005	18:00	4.8	3158	19.1	8.05	25.6	29	158	0.8
4/18/2005	19:00	1.6	3095	18.4	8.04	22.5	38	17	1.6
4/18/2005	20:00	1.2	3044	17.8	8.07	19.2	52	0	2.2
4/18/2005	21:00	1.4	3013	17.3	8.07	16.6	61	0	2.1
4/18/2005	22:00	1.2	2990	17.0	8.07	15.5	67	0	1.7
4/18/2005	23:00	0.9	2972	16.8	8.09	14.5	69	0	1.3
4/18/2005	0:00	0.8	2919	16.6	8.08	13.1	72	0	0.8
4/19/2005	1:00	0.6	2765	16.4	8.10	12.6	71	0	1.0
4/19/2005	2:00	0.5	2683	16.3	8.10	11.5	74	0	0.7
4/19/2005	3:00	0.5	2601	16.2	8.11	10.3	79	0	0.4
4/19/2005	4:00	0.4	2510	16.0	8.10	9.8	83	0	0.5
4/19/2005	5:00	0.4	2439	16.0	8.10	8.9	87	0	0.7
4/19/2005	6:00	0.4	2407	15.9	8.09	9.0	88	8	0.8
4/19/2005	7:00	0.4	2460	15.8	8.09	10.4	84	115	1.0
4/19/2005	8:00	0.4	2780	16.0	8.10	14.5	69	327	1.4
4/19/2005	9:00	0.4	2951	16.5	8.12	18.8	54	491	1.4
4/19/2005	10:00	0.3	3055	17.9	8.10	21.6	49	684	1.7
4/19/2005	11:00	0.4	3074	18.1	8.10	23.8	45	789	1.8

^a Measured at depth of ~6-7cm

^b Measured at 2m height above surface

^c RH = Relative Humidity

^d SR = Solar Radiation

^e WS = Wind Speed measured at 10m height above surface

Appendix 8. Experimental hourly averaged lagoon flux measurements, meteorological and lagoon parameters for Summer 2005.

Date	Time	H ₂ S Flux μg m ² min ⁻¹	NH ₃ -N Flux μg m ² min ⁻¹	Lagoon Temp ^a Celcius	pH ^a	Air Temp ^b Celcius	RH ^c %	SR ^d W m ⁻²	WS ^e m s ⁻¹
6/14/2005	12:00	1.5		30.1	8.08	30.6	66	884	2.1
6/14/2005	13:00	1.6		30.0	8.10	31.0	66	707	2.1
6/14/2005	14:00	1.5		31.5	8.10	31.9	61	784	2.6
6/14/2005	15:00	1.1		32.1	8.09	32.2	58	739	2.9
6/14/2005	16:00	1.0		31.6	8.09	32.3	58	579	2.6
6/14/2005	17:00	1.1		31.2	8.08	32.4	58	412	2.4
6/14/2005	18:00	1.0		30.8	8.09	31.7	60	219	1.6
6/14/2005	19:00	0.8		30.7	8.09	30.4	68	69	0.8
6/14/2005	20:00	1.3		30.7	8.06	28.6	77	4	0.4
6/14/2005	21:00	2.8		30.5	8.04	27.6	82	0	2.3
6/14/2005	22:00	3.7		30.0	8.02	27.2	84	0	2.8
6/14/2005	23:00	3.8		29.7	8.02	26.6	87	0	2.4
6/14/2005	0:00	4.6		29.5	8.02	26.1	87	0	2.4
6/15/2005	1:00	6.7		29.3	8.03	25.5	89	0	2.2
6/15/2005	2:00	7.5		29.1	8.02	25.0	91	0	1.9
6/15/2005	3:00	6.8		28.9	8.01	24.7	92	0	1.9
6/15/2005	4:00	8.1		28.7	8.03	24.5	93	0	1.9
6/15/2005	5:00	7.0		28.5	8.03	24.6	93	1	2.2
6/15/2005	6:00	6.5		28.4	8.03	24.7	93	43	1.7
6/15/2005	7:00	5.4		28.3	8.01	25.9	88	220	2.1
6/15/2005	8:00	3.3		28.6	8.05	28.0	78	432	2.2
6/15/2005	9:00	1.4		29.1	8.06	30.0	68	615	2.4
6/15/2005	10:00	1.7		29.2	8.05	31.4	61	761	2.4
6/15/2005	11:00			29.8	8.05	32.5	59	842	2.3
6/15/2005	12:00	2.9		30.4	8.05	33.2	57	924	2.7
6/15/2005	13:00	3.1		31.5	8.00	33.8	54	875	2.5
6/15/2005	14:00	2.1		31.7	7.99	34.1	52	749	2.3
6/15/2005	15:00	2.2		31.9	7.99	34.5	48	785	2.8
6/15/2005	16:00	2.6		32.0	7.98	34.4	46	602	2.8
6/15/2005	17:00	3.2		31.9	7.99	34.3	47	417	2.0
6/15/2005	18:00	1.9		31.9	8.01	31.7	59	77	0.7
6/15/2005	19:00	6.9		31.5	8.01	26.9	77	59	2.8
6/15/2005	20:00	3.4		31.2	8.00	25.3	90	3	0.5
6/15/2005	21:00	4.4		30.9	7.93	25.6	91	0	0.5
6/15/2005	22:00	2.2		30.7	8.02	25.5	90	0	0.6
6/15/2005	23:00	4.9		30.5	8.00	24.4	95	0	0.6
6/15/2005	0:00	6.2		30.3	7.97	24.1	95	0	0.6
6/16/2005	1:00	5.7		30.1	7.96	23.7	95	0	0.5
6/16/2005	2:00	7.9		29.9	7.95	23.0	95	0	0.6
6/16/2005	3:00	10.1		29.7	7.94	22.7	96	0	0.6
6/16/2005	4:00	9.7		29.5	7.94	22.2	96	0	0.4
6/16/2005	5:00	8.1		29.2	7.95	21.6	97	1	0.5
6/16/2005	6:00	9.3		29.2	7.93	21.8	97	68	0.6

Appendix 8 (cont). Experimental hourly averaged lagoon flux measurements, meteorological and lagoon parameters for Summer 2005.

6/16/2005	7:00	7.6		29.1	7.93	24.0	91	235	0.7
6/16/2005	8:00	7.6		29.2	7.92	26.6	72	447	1.3
6/16/2005	9:00	7.5		29.2	7.90	27.9	58	628	1.8
6/16/2005	10:00	5.4		29.6	7.92	29.1	50	783	1.9
6/16/2005	11:00	13.3	4604	30.4	7.94	30.1	45	883	1.9
6/16/2005	12:00	12.2	4589	30.7	7.93	31.2	42	933	1.7
6/16/2005	13:00	8.3	4709	31.3	7.93	31.6	41	928	1.9
6/16/2005	14:00	3.4	4872	32.0	7.93	32.0	39	820	1.8
6/16/2005	15:00	3.5	4905	32.1	7.95	31.7	40	633	1.7
6/16/2005	16:00	3.8	4985	32.5	8.00	31.5	39	521	2.0
6/16/2005	17:00	3.9	4900	32.1	8.00	31.0	40	419	1.8
6/16/2005	18:00	4.3	4764	31.5	8.02	30.3	43	271	1.5
6/16/2005	19:00	6.4	4668	31.1	7.99	27.9	54	90	0.5
6/16/2005	20:00	8.0	4621	30.9	7.96	25.0	68	4	0.1
6/16/2005	21:00	8.5	4556	30.6	7.96	23.1	76	0	0.4
6/16/2005	22:00	8.9	4516	30.4	7.96	21.8	81	0	0.4
6/16/2005	23:00	11.6	4451	30.1	7.95	21.1	82	0	0.4
6/16/2005	0:00	11.9	4419	29.9	7.95	20.7	89	0	0.4
6/17/2005	1:00	11.9	4339	29.5	7.96	21.6	77	0	1.2
6/17/2005	2:00	9.2	4292	29.2	7.97	22.4	63	0	1.4
6/17/2005	3:00	9.2	4235	28.9	7.98	21.0	70	0	1.0
6/17/2005	4:00	10.2	4191	28.7	7.98	20.1	72	0	1.0
6/17/2005	5:00	11.8	4153	28.5	7.98	19.9	70	1	1.0
6/17/2005	6:00	12.0	4103	28.2	7.98	19.4	74	55	0.6
6/17/2005	7:00	10.0	4083	28.1	7.98	20.4	70	200	1.2
6/17/2005	8:00	7.6	4074	28.0	7.99	21.6	67	277	1.8
6/17/2005	9:00	6.6	4059	27.9	8.03	22.6	65	364	2.0
6/17/2005	10:00	5.6	4062	28.0	8.07	23.4	61	323	2.0
6/17/2005	11:00			28.3	8.04	24.3	57	580	2.3
6/17/2005	12:00	3.6	4200	28.9	8.03	25.7	52	896	2.4
6/17/2005	13:00	3.3	4238	29.1	8.00	26.5	51	681	1.6
6/17/2005	14:00	2.0	4247	29.1	7.98	27.1	52	651	1.4
6/17/2005	15:00	2.9	4306	29.5	7.97	27.5	54	567	1.3
6/17/2005	16:00	2.5	4425	30.1	8.00	28.4	49	621	1.2
6/17/2005	17:00	2.4	4449	30.2	7.98	28.4	48	454	1.3
6/17/2005	18:00	2.0	4429	30.1	7.99	27.8	51	247	1.1
6/17/2005	19:00	1.8	4334	29.6	8.06	25.7	65	81	0.6
6/17/2005	20:00	3.0	4239	29.1	8.01	23.6	75	4	0.8
6/17/2005	21:00	3.6	4195	28.9	7.99	21.4	88	0	0.3
6/17/2005	22:00	4.4	4143	28.6	7.98	20.2	92	0	0.1
6/17/2005	23:00	4.5	4109	28.4	7.97	19.3	95	0	0.4
6/17/2005	0:00	4.8	4080	28.2	7.97	18.9	96	0	0.5
6/18/2005	1:00	6.1	4036	28.0	7.96	18.2	96	0	0.2
6/18/2005	2:00	6.1	4003	27.8	7.96	17.5	96	0	0.2
6/18/2005	3:00	4.7	3958	27.5	7.96	16.7	97	0	0.5
6/18/2005	4:00	4.8	3936	27.4	7.96	15.9	97	0	0.5
6/18/2005	5:00	4.9	3899	27.2	7.96	15.6	97	1	0.4
6/18/2005	6:00	5.2	3867	26.9	7.96	15.8	97	57	0.3

Appendix 8 (cont). Experimental hourly averaged lagoon flux measurements, meteorological and lagoon parameters for Summer 2005.

6/18/2005	7:00	4.7	3864	26.9	7.97	17.5	96	171	0.7
6/18/2005	8:00	3.8	3885	27.0	8.00	20.3	84	278	0.8
6/18/2005	9:00	2.6	3909	27.2	8.01	23.2	70	479	1.2
6/18/2005	10:00	3.3	3934	27.3	7.98	24.9	60	548	1.8

^a Measured at depth of ~6-7cm

^b Measured at 2m height above surface

^c RH = Relative Humidity

^d SR = Solar Radiation

^e WS = Wind Speed measured at 10m height above surface

Appendix 9. Characterization of Non-Methane Volatile Organic Compounds at Swine Facilities in Eastern North Carolina

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Samples were collected and analyzed in a field study to characterize C₂-C₁₂ volatile organic compounds (VOCs) emitted at six swine facilities in Eastern North Carolina between April 2002 and March 2003. Two sites employed conventional lagoon and field spray technologies, while four sites utilized various alternative waste treatment technologies in an effort to substantially reduce gaseous compound emissions, odor, and pathogens from these swine facilities. More than 100 compounds, including various paraffins, olefins, aromatics, ethers, alcohols, aldehydes, ketones, halogenated hydrocarbons, phenols, and sulfides were positively identified and quantified by Gas Chromatographic/Flame Ionization Detection (GC/FID) analysis and confirmed by Gas Chromatographic/Mass Spectrometry (GC/MS). GC/MS analysis of one particularly complex sample collected assisted in providing identification and retention times for 17 sulfur type VOCs including dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide as well as many other VOCs. Highest VOC concentration levels measured at each of the facilities were near the hog barn ventilation fans. Total measured VOCs at the hog barns were typically dominated by oxygenated hydrocarbons (HCs), i.e., ethanol, methanol, acetaldehyde, and acetone. These compounds, in addition to other oxygenated VOCs measured at the various sites, generally represented ~37-73% of net total measured VOCs that were emitted from the hog barns at the various sites. Dimethyl sulfide and dimethyl disulfide, both recognized as malodorous compounds, were determined to have higher concentration levels at the barns than the background at every farm sampled with the exception of one farm during the warm sampling season.

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Methods and Technology
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Appendix 10. Dynamic Chamber System to Measure Gaseous Compounds Emissions and Atmospheric-Biospheric Interactions

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Dynamic flow-through chamber system has been developed in response to a need to measure emissions of nitrogen and sulfur compounds for a variety of field applications. The cylindrical chamber system is constructed of chemically inert materials and internally lined with 5mil thick transparent fluorinated ethylene polypropylene (FEP) Teflon to reduce chemical reactions and build up of temperature inside the chamber. The chamber (diameter = 27cm, height = 42 cm, volume = 24.05 L) is designed with an open-ended bottom that can penetrate either soil or liquid to a depth of ~6-8 cm, thus creating a completely enclosed system. Carrier gas (e.g. compressed zero-grade air) is pumped at a constant flow rate (~2 to ~5 lpm), depending on the season. The air inside the chamber is well mixed by a variable-speed, motor-driven Teflon impeller (~40 to ~100 rpm). Many different laboratory and field experiments have been conducted using this dynamic chamber system. Oxides of nitrogen (NO , NO_2 , NO_y) emissions have been measured from agricultural soils where nitrogen-rich fertilizers have been applied. Ammonia-nitrogen ($\text{NH}_3\text{-N}$) and reduced organic sulfur compounds emissions have been measured using this same technique across a gas-liquid interface at swine waste treatment anaerobic storage lagoons, and agricultural fields. The chamber system has also been deployed to measure uptake of nitrogen and hydrogen peroxide gases by crops and vegetation to examine atmospheric-biospheric interactions. Emissions measurements have been validated by a coupled gas-liquid transfer with chemical reaction model as well as a U.S. Environmental Protection Agency (EPA) WATER 9 model.

Presented at:

NATO Advanced Research Workshop
Environmental Simulation Chambers: Application to Atmospheric Chemical Processes
Zakopane, Poland, October 1 – 4, 2004

Appendix 11. Measurement and Analysis of Ammonia and Hydrogen Sulfide Emissions from an Anaerobic Swine Waste Treatment Lagoon and Confinement Building in North Carolina

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Emissions of atmospheric ammonia-nitrogen ($\text{NH}_3\text{-N}$, where $\text{NH}_3\text{-N} = (14/17)\text{NH}_3$) and hydrogen sulfide (H_2S) from a commercial anaerobic swine waste treatment lagoon ($30,630 \text{ m}^2$) and a fan-ventilated swine confinement building located next to the lagoon were measured over a one year period. Continuous simultaneous measurements were made at the lagoon using a dynamic flow-through chamber system for ~ 1 week during four seasons, Oct-Nov 2004 (fall), February 2005 (winter), April 2005 (spring), and June 2005 (summer) in an effort to examine diurnal and seasonal variability and the respective relationships of $\text{NH}_3\text{-N}$ and H_2S emissions to lagoon physiochemical properties. Continuously measured lagoon physiochemical parameters include lagoon surface temperature and lagoon pH. Lagoon samples were collected daily and analyzed for Total Kjeldahl Nitrogen (TKN), Total Ammoniacal Nitrogen (TAN), and total sulfide concentration (mg L^{-1}). TKN, TAN, and sulfide concentrations ranged from 400-650, 360-590, and 0.1-13.0 mg L^{-1} , respectively. For $\text{NH}_3\text{-N}$, the largest fluxes were observed during the summer ($\sim 4200 \mu\text{g N m}^{-2} \text{ min}^{-1}$). During the fall and spring, average $\text{NH}_3\text{-N}$ fluxes were 1634 ± 505 and $2495 \pm 465 \mu\text{g N m}^{-2} \text{ min}^{-1}$, respectively. The lowest fluxes were observed during the winter where average flux values were $1290 \pm 246 \mu\text{g N m}^{-2} \text{ min}^{-1}$. The lowest fluxes for H_2S were also observed during the winter season, $\sim 0.0 \mu\text{g m}^{-2} \text{ min}^{-1}$. Average fluxes increased during the fall ($0.3 \pm 0.1 \mu\text{g m}^{-2} \text{ min}^{-1}$) and spring (0.5 ± 1.0) and were observed at highest flux values during the summer ($5.3 \pm 3.2 \mu\text{g m}^{-2} \text{ min}^{-1}$). Generally, the lagoon emissions for H_2S were ~ 3 -4 orders of magnitude less than $\text{NH}_3\text{-N}$.

Continuous simultaneous $\text{NH}_3\text{-N}$ and H_2S emissions from a swine confinement house were also made for ~ 1 week period immediately prior to or following the lagoon experiments. Static pressure inside the building, fan flow rates (calculated from measured rpms and from manufacturer's fan discharge tables), and barn temperature at the fan outlets were measured continuously. $\text{NH}_3\text{-N}$ emissions were highest in spring ($49691 \pm 19518 \mu\text{g N min}^{-1} 1000\text{kg live animal weight}^{-1} (\text{LAW})$) and lowest during summer ($19122 \pm 12057 \mu\text{g N min}^{-1} 1000\text{kg LAW}^{-1}$). H_2S emissions were also lowest in summer ($2466 \pm 1515 \mu\text{g min}^{-1} 1000\text{kg LAW}^{-1}$) but were observed to be highest during the winter

Appendix 11 (cont). Measurement and Analysis of Ammonia and Hydrogen Sulfide Emissions from an Anaerobic Swine Waste Treatment Lagoon and Confinement Building in North Carolina

season ($7119 \pm 2796 \mu\text{g min}^{-1} 1000\text{kg LAW}^{-1}$). During the summer, the house had been cleaned three weeks prior to the experiment, which may account for the lower emissions.

Presented at:

Agricultural Air Quality: State of the Science Workshop
Potomac, MD, June 5 – 8, 2006

Appendix 12. Measurement and Modeling of Hydrogen Sulfide Emissions Across the Gas-Liquid Interface of an Anaerobic Swine Waste Treatment Lagoon

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Hydrogen sulfide (H_2S) 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 US, anaerobic waste treatment lagoons are widely used to store and treat hog excreta at commercial hog farms. Environmental concerns and complaints regarding air and water quality associated with the increased number of animals and management of subsequent wastes accompanying the growth of this industry has been considerable. However, due to a lack of intensive measurement initiatives, emissions of hydrogen sulfide from anaerobic waste treatment lagoons have not been well quantified.

Under anaerobic conditions, any excreted sulfur that is not in the form of H_2S (i.e., certain amino acids) will be reduced microbially to produce H_2S and so manures managed as liquids or slurries are potential sources of hydrogen sulfide emissions. The magnitude of H_2S emissions in this type of environment is a function of liquid phase concentration, temperature, pH and meteorological parameters. In aqueous form, H_2S exists in equilibrium with the bisulfide anion (HS^-) and sulfide anion (S^{2-}). Temperature and pH affect the solubility of H_2S in water. The solubility of H_2S in water increases at pH values above 7, so as pH shifts from alkaline to acidic ($\text{pH} < 7$), the potential for H_2S emissions increases.

The process of hydrogen sulfide emissions from anaerobic waste treatment lagoons are investigated using a Coupled Mass Transfer with Chemical Reactions Model. This model is based on the concept of simultaneous mass transfer and equilibrium chemical reactions. Both aqueous phase and gas phase reactions are considered. A sensitivity analysis was performed and model results were compared with hydrogen sulfide fluxes measured at a commercial swine finishing farm waste treatment storage lagoon in North Carolina using a dynamic emission flux chamber system. The measurements were made continuously for ~5 day increments over all four seasons so that diurnal and seasonal variations were established. Experimental results will be utilized to evaluate the model's accuracy in calculating lagoon hydrogen sulfide emissions.

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Potomac, MD, June 5 – 8, 2006