ABSTRACT

RUMSEY, IAN COOPER. Characterizing Reduced Sulfur Compounds and Non-Methane Volatile Organic Compounds Emissions from a Swine Concentrated Animal Feeding Operation. (Under the direction of Viney P. Aneja.)

Reduced sulfur compounds (RSCs) and non-methane volatile organic compounds (NMVOCs) emissions from concentrated animal feeding operations (CAFOs) have become a potential environmental and human health concern. Both RSCs and NMVOCs contribute to odor. In addition, RSCs also have the potential to form fine particulate matter (PM_{fine}) and NMVOCs the potential to form ozone.

Measurements of RSCs and NMVOCs emissions were made from both an anaerobic lagoon and barn at a swine CAFO in North Carolina. Emission measurements were made over all four seasonal periods. In each seasonal period, measurements were made from both the anaerobic lagoon and barn for ~1 week. RSC and NMVOCs samples were collected using passivated canisters. Nine to eleven canister samples were taken from both the lagoon and barn over each sampling period. The canisters were analyzed ex-situ using gas chromatography flame ionization detection (GC-FID). Hydrogen sulfide (H_2S) measurements were made in-situ using a pulsed fluorescence H_2S/SO_2 analyzer. During sampling, measurements of meteorological and physiochemical parameters were made.

H_2S had the largest RSC flux, with an overall average lagoon flux of 1.33 $\mu g\ m^{-2}\ min^{-1}$. The two main RSCs identified by the GC-FID, dimethyl sulfide (DMS) and dimethyl disulfide (DMDS), had overall average lagoon fluxes an order of magnitude lower, 0.12 and 0.09 $\mu g\ m^{-2}\ min^{-1}$, respectively. Twelve significant NMVOCs were

identified in lagoon samples (ethanol, 2-ethyl-1-hexanol, methanol, acetaldehyde, decanal, heptanal, hexanal, nonanal, octanal , acetone, methyl ethyl ketone, and 4-methylphenol). The overall average fluxes for these NMVOCs, ranged from 0.08 μg m^{-2} min^{-1} (4-methylphenol) to 2.11 μg m^{-2} min^{-1} (acetone).

Seasonal H_2S barn concentrations ranged from 72-631 ppb. DMS and DMDS seasonal concentrations were 2-3 orders of magnitude lower. There were six significant NMVOCs identified in barn samples (methanol, ethanol, acetone 2-3 butanedione, acetaldehyde and 4-methylphenol). Their overall average NMVOCs concentrations ranged from 2.87 ppb (4-methylphenol) to 16.21 ppb (ethanol). The overall average barn normalized emissions were 3.3 g day^{-1} AU^{-1} (AU (animal unit) = 500 kg) for H_2S, 0.018 g day^{-1} AU^{-1} for DMS and 0.037 g day^{-1} AU^{-1} for DMDS. Normalized overall average NMVOC emissions ranged from 0.45 g day^{-1} AU^{-1} for ethanol to 0.16 g day^{-1} AU^{-1} for acetaldehyde. Barn H_2S concentrations were generally one to two orders of magnitude above their odor thresholds. DMDS concentrations also regularly exceeded the lower limit of an odor threshold. Four NMVOCs (2-3 butanedione, decanal, 4-methylphenol and nonanal) had barn concentrations exceeding an odor threshold.

Using overall average lagoon and barn emissions, the emissions from swine CAFOs in North Carolina were estimated. H_2S had the largest RSC emission with an estimated North Carolina emission of 1.46 million kg yr^{-1}, which was ~21% of total North Carolina H_2S emissions. Ethanol was the NMVOC with the largest North Carolina emission with an emission of 206,367 kg yr^{-1}.

H_2S manure emissions were modeled using a process based air-manure interface (A-MI) mass transfer model. Different approaches were used to calculate the three main components of the A-MI mass transfer model: the dissociation constant, the Henry's law constant and the overall mass transfer coefficient. The A-MI mass transfer model performed fairly well in comparison to 15 minute average lagoon fluxes ($r^2 = 0.57$, $p<0.0001$) and seasonal lagoon fluxes. It is hypothesized that with appropriate information on the overall mass transport coefficient, that the model could be applied to predict CAFO trace gas emissions from different manure surfaces, therefore providing a method for quantifying emissions in different production, management and environmental conditions.

Characterizing Reduced Sulfur Compounds and Non-Methane Volatile Organic Compounds Emissions from a Swine Concentrated Animal Feeding Operation

by
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BIOGRAPHY

Ian Rumsey was born in Leyton, United Kingdom on the 12th December 1979 to Andrew and Pauline Rumsey. Ian lived his childhood years in Loughton, Essex, where until the age of 16 he attended Roding Valley High School. Here he first started to develop an interest in math, science and the environment. He then attended Epping Forest College where he embarked on A-levels in math, physics and geography.

Upon graduation, Ian attended Kingston University in the United Kingdom studying environmental science and geology. He graduated with a B.S in Earth Science with first class honors in 2001. During his undergraduate degree, Ian developed a particular interest in air pollution, which resulted in him starting a Master's of science program in atmospheric science at North Carolina State University. For his Masters research, Ian investigated ammonia emissions from hog farms as part of a State of North Carolina study (project OPEN: Odor, Pathogens, and Emissions of Nitrogen).
After graduating his master's in 2004, Ian continued to work on project OPEN as a research scientist for one year.

In the fall of 2005, he started his Ph.D in the same program as his masters. His research continued to focus on the subject area of agricultural air quality, focusing on reduced sulfur compound and non-methane volatile organic compound emissions from hog farms. Upon completion of his Ph.D, Ian will work as a post-doc with Dr. John Walker of the U.S. EPA.

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CHAPTER I. INTRODUCTION

The intensification of animal agriculture to meet the food demands of an increasing world population, have resulted in a number of environmental concerns. These concerns include emissions of nitrogen, sulfur and volatile organic compounds and particulate matter from concentrated animal feeding operations (CAFOs) into the atmosphere (Aneja et al., 2008).

Swine CAFOs are a primary agricultural industry in the State of North Carolina, producing revenues of over $2 billion per year. It is estimated that approximately two-thirds of North Carolina's swine population of 10 million resides in six adjacent counties in eastern North Carolina (Figure 1.1).The swine industry in North Carolina started developing rapidly in the late 1980's. Between 1987 and 1997, the swine population increased from 2.5 million to 10 million (NCDA, 2007). The population then stabilized as a result of a moratorium, which did not allow the building of any new swine farms or the expansion of existing farms, unless a set of more restrictive environmental criteria's could be met. As the result of the growth of the swine CAFOs, there are significant environmental concerns.

Scientific studies of swine CAFO emissions of ammonia (e.g. Aneja et al., 2001; Heber et al., 2000; Zhu et al., 2000; Lim et al., 2004; Harper et al., 2000) and methane (e.g. Sharpe et al., 2002; Sharpe and Harper, 1999; Safley and Westerman, 1988; Pos et al., 1985) have been well documented. However, emissions of reduced sulfur compounds (RSCs) and non-methane volatile organic compounds (NMVOCs) have not been studied

as extensively. Emissions of RSCs and NMVOCs are an important concern locally, as RSCs and certain NMVOCs contribute to odor. Emissions of odorous compounds are important as they can cause health symptoms and additionally health effects (Schiffman and Williams, 2005). Furthermore they can affect the quality of life for people in surrounding areas (Wing and Wolf, 2000; Thu et al., 1997).

There are also potential regional environmental effects associated with RSC and NMVOC emissions. RSCs can react in the atmosphere to form sulfur dioxide (SO_2), which can in turn react to form ammonium sulfate or ammonium bi-sulfate particulate matter. Particulate matter in the form of PM_{fine} (particulate matter with an aerodynamic diameter equal or less than 2.5 μm) can affect human health through damage to the lungs (Samet et al., 2000; U.S. EPA, 1997a). Particulate matter can also additionally impair visibility (Malm et al., 2004; Seinfeld and Pandis, 1998) and scatter incoming solar radiation resulting in regional cooling (Lovelock et al., 1972).

NMVOCs are generally reactive, and can through a set of reactions form ozone. Ozone can have negative impacts on human's respiratory system, reducing lung capacity and increasing the development of illnesses such as asthma (Lippmann, 1993).

H_2S is the most studied of the RSCs and NMVOCs, with many studies in Midwest of the U.S. reporting H_2S swine CAFO emissions (Heber et al., 1997; Ni et al., 2002; Zhu et al., 2000; Jacobson et al., 2003; Jacobson et al., 2004; Heber et al., 2004; Zahn et al., 2001, Lim et al., 2003, Byler et al., 2004). However, due to differences in production, management, and environmental conditions, there must also be comprehensive measurements of North Carolina H_2S swine CAFO emissions. Presently, North Carolina

H_2S swine CAFO emissions has not been studied extensively. Blunden et al. (2008) and Blunden and Aneja (2008) are the only known studies that have measured H_2S emissions from a swine CAFO in North Carolina. Therefore, further measurements are needed to assess the magnitude of H_2S emissions and the effects of production, management and environmental conditions.

As mentioned, H_2S swine CAFO emissions vary due to difference in production, management and environmental conditions. Therefore there is a need for a process based model, to provide a method for quantifying H_2S manure emissions in these different conditions.

In comparison to H_2S, measurements of concentrations and emissions of RSCs (Clanton and Schmidt, 2000; Blunden et al., 2005; Kim et al., 2007; Trabue et al., 2008a) and NMVOCs (Blunden et al., 2005; Trabue et al., 2008b; Zahn et al., 1997; Schiffman et al., 2001) have been limited. There have been no known studies that have reported RSC and NMVOC emissions from a swine CAFO with respect to seasonal and environmental variations.

1.1. BACKGROUND

1.1.1. Global Sulfur Cycle

Sulfur is estimated to be present in the earth's crust at a mixing ratio of less than 500 ppm by mass. Through a combination of natural and anthropogenic emissions, the earth's atmosphere sulfur volume mixing ratio is less than 1ppm (Seinfield and Pandis, 1998). This concentration may seem low but sulfur-containing compounds are known to have a significant influence on atmospheric chemistry and climate (Seinfield and Pandis,

1998). There are seven main sulfur gases in the sulfur cycle; these are hydrogen sulfide (H_2S), dimethyl sulfide (CH_3SCH_3), dimethyl disulfide (CH_3SSCH_3), carbonyl sulfide (COS), carbon disulfide (CS_2), methyl mercaptan (CH_3SH), and sulfur dioxide (SO_2).

Three studies' (Schlesinger, 1997; Warneck, 1988; Seinfield and Pandis, 1998) estimates of global sulfur sources and sinks are presented in Table 1.1. In comparison the three global sulfur cycles are in fairly good agreement. Warneck's (1988) estimation of global sulfur sources/sinks is slightly higher (306 Tg S yr^{-1}) than Schlesinger's (1997) estimation (270 Tg S yr^{-1}). Additionally, the Seinfield and Pandis (1998) study would be of a similar magnitude to the other two studies, if sea spray estimates were included. A diagram of Schlesinger's (1997) global sulfur cycle is also presented in Figure 1.2, which shows the estimates of sulfur transportation, as well as the various sources and sinks.

Anthropogenic emissions mainly consist of SO_2 through fossil fuel burning and industrial activities (Finlayson-Pitts and Pitts, 2000, Andreae, 1990), and are estimated to emit 73-106 Tg S yr^{-1} (Schlesinger, 1997; Warneck, 1988; Seinfield and Pandis, 1998)

Natural emission sources include volcanoes, sea spray, and a variety of sources that originate from biogenic processes. Volcanic eruptions emit large amounts of SO_2 and smaller quantities of H_2S and CH_3SCH_3. It is estimated that volcanoes emit between 7-11.8 Tg S yr^{-1} (Schlesinger, 1997; Warneck, 1988; Seinfield and Pandis, 1998).

Sea spray is estimated to be the largest natural emission source. Sea spray is largely composed of sulfates (SO_4^{-2}) (Finlayson-Pitts and Pitts, 2000) and is estimated to emit between 144-150 Tg yr^{-1} (Schlesinger, 1997; Warneck, 1988). Biogenic processes emit RSCs including H_2S, CS_2, CH_3SCH_3, CH_3SSCH_3, and CH_3SH from both land and

the oceans. The oceans are estimated to be a larger biogenic source than land. Ocean emission estimates range from 6-36 Tg S yr^{-1} (Schlesinger, 1997; Warneck, 1988; Seinfield and Pandis, 1998), whereas land emissions range from 4-7 Tg S yr^{-1} (Schlesinger, 1997; Warneck, 1988; Seinfield and Pandis, 1998).

1.1.2. Biogenic RSC Production

Sulfate is the main form of sulfur in the global environment. In order for there to be biogenic emissions of sulfur compounds there has to be a reduction of sulfate. There are two types of processes that can lead to sulfate reduction (in the biosphere, hydrosphere and lithosphere). These processes are assimilatory sulfate reduction and dissimilatory sulfate reduction (Andreae, 1990).

Assimilatory sulfate reduction can occur as waste decomposes. As it decomposes anaerobically the bacteria produces cell biosynthesis of amino acids such as methionine, and cysteine. Metabolism of these sulfur containing amino acids results in the production of ammonia, sulfides, and mercaptans. Examples are shown in the following reactions (Mackie et al., 1998):

$$\text{Cysteine} \rightarrow \text{Pyruvate} + NH_3 + H_2S \quad (1)$$

$$\text{Methionine} \rightarrow \text{Pyruvate} + NH_3 + CH_3SH \quad (2)$$

Bacteria that are involved in the assimilatory process are the genera *Megasphaera*, *Veillonella*, and enterobacteria (Mackie et al., 1998).

Dissimilatory sulfate reduction is used by bacteria to obtain thermodynamic energy in an oxygen-depleted environment. Molecular oxygen is the thermodynamically

preferred electron acceptor, but in an anoxic environment where sulfate exceeds oxygen, these will be used as electron acceptors. Sulfate can be supplied in two different ways, either by diet or by the processes of depolymerization and desulfation of sulfated glycoproteins. In the stomachs of animals the major sulfate reducer is the genus *Desulfovibrio* (Mackie et al., 1998). This process can result in the release of H_2S and other RSCs (Andreae, 1990).

Additionally in anoxic environments, a process known as methylation has been found to occur, which can lead to production of Methyl Mercaptan and dimethyl sulfide. This is shown in the following set of reactions (Bentley and Chasteen, 2004):

$$R\text{-}O\text{-}CH_3 + H_2S \rightarrow R\text{-}OH + CH_3\text{-}SH \quad (3)$$

$$R\text{-}O\text{-}CH_3 + CH_3\text{-}SH \rightarrow R\text{-}OH + CH_3\text{-}S\text{-}CH_3 \quad (4)$$

Kiene and Hines (1995) examined the methylation of CH_3-SH in anoxic *Sphagnum* peat, and concluded from their results that this mechanism is a major pathway for biogenic production of dimethyl sulfide.

Decomposition by bacteria of the amino acid, Methionine can lead to the production of dimethyl disulfide through the processes of oxidative deamination followed by demethiolation (Kadota and Ishida, 1972):

$$\text{Methionine} \rightarrow \alpha\text{-Ketomethionine} + NH_3 \quad \text{(oxidative deamination)} \quad (5)$$

$$\alpha\text{-Ketomethionine} \rightarrow \alpha\text{-Ketobutyric acid} \quad \text{(demethiolation)} \quad (6)$$

$$\alpha\text{-Ketobutyric acid} + (CH_3)\text{-}SH \rightarrow CH_3\text{-}SS\text{-}CH_3$$

Additionally CS_2 can source from the biogenic environment. Spoelstra et al., (1980) comments that sulfate reducing bacteria has been found to produce trace emissions of CS_2. It is also reported that CS_2 is a product from cysteine.

1.1.3. The Global Carbon Cycle

The global carbon cycle describes the exchanges of carbon between the four major reservoirs. A simplified modern version of the global carbon cycle is shown in Figure 1.3. Carbon is released into the atmosphere from three different sources. There are biogenic emissions through the processes of respiration and decomposition, ocean emissions as a result of diffusion, and anthropogenic emissions, through mainly fossil fuel burning. Through photosynthesis, some of the anthropogenic carbon is taken in by vegetation. This sink though is not as large as the source from anthropogenic activities, resulting in a net accumulation of carbon in the atmosphere. The majority of this carbon in the atmosphere is CO_2. Other carbon cycle compounds include carbon monoxide (CO) and methane (CH_4). Methane has a atmospheric concentration of ~1750 ppb and an atmospheric lifetime of ~9 years (Schlesinger, 1997). However, there are organic compounds that are emitted in smaller amounts; this includes a group of compounds known as non-methane volatile organic compounds (NMVOCs).

1.1.4. Non-Methane Volatile Organic Compounds (NMVOCs)

A NMVOC is a compound that contains the element carbon, expect for methane. In this study, this terms excludes sulfur compounds that contain carbon (e.g., dimethyl sulfide) to avoid confusion. Koppmann (2007) defines a volatile organic compound as

having 15 or less carbon atoms, a boiling point up to 260^{o}C and a vapor pressure greater than 10 pa at 25^{o}C. This study focuses on NMVOC in the C_2-C_{12} range, as these are the major NMVOC that are typically found in the ambient atmosphere. There are thousands of NMVOC emitted from both biogenic and anthropogenic sources.

1.1.4.1. *Global NMVOCs Emissions*

A summary of global sources and emissions of NMVOCs, as well as the main compounds groups and compounds contributing to these emissions is provided in Table 1.2. Anthropogenic emissions are responsible for approximately 10% of global NMVOCs (Warneck, 2000). Anthropogenic sources include various industries such as the petroleum industry, the chemical industry, the natural gas industry and the organic solvent industry. Petroleum-related sources release 36-62 Tg yr^{-1} and are largely composed of alkanes alkenes , and aromatic compounds, including ethylene, toluene, benzene, m-p-xylene, i-pentene, n-pentane, n-butane, and i-butane (Warneck, 2000; Nelson et al, 1983)

Natural gas emissions are considerably smaller than petroleum related emissions, around 2-14 Tg yr^{-1} (Warneck, 2000) The compounds emitted are mainly light alkanes, with the largest compound emissions being ethane, propane, n-pentane, and i-pentane (Warneck, 2000; Nelson et al, 1983). Organic solvents emissions are of a similar magnitude to natural gas emissions, with an estimated emission rate of 8-20 Tg yr^{-1}. Organic solvents emit heavy alkanes and aromatic compounds such as toluene, ethanol and m-p xylene (Warneck, 2000; Nelson et al, 1983).

Biomass burning is also a large anthropogenic source emitting 25-80 Tg yr^{-1}. Radke et al. (1991) identified the major compounds as being ethane, propane, propene and acetylene.

Biogenic processes emit NMVOCs from land, oceans and soil and are responsible for approximately 90% of the total emissions of NMVOC. Plants are the largest biogenic source of NMVOC, with an estimated rate of 812-1493 Tg yr^{-1} (Warneck, 2000). There are thousands of organic compounds in plants, but due to plant structure it is estimated that approximately 40 are emitted at rates that could affect the chemistry of the atmosphere (Guenther et al., 2000). The main NMVOC emitted is isoprene. Isoprene emissions are highest from deciduous trees (Koppman, 2007). Other main compounds emitted include the chemical group monoterpenes. The largest emitters of this chemical group are α- Pinene and β- Pinene. These emissions are highest from coniferous trees such as pine and fir (Koppman, 2007).On a smaller scale alkenes, alkanes, aldehydes, alcohols, ketones, esters, and organic acids are also produced (Guenther et al.,2000; Warneck, 2000). According to a study in North America (Guenther et al., 2000), the most prominent of these compounds in descending order of magnitude are methanol, ethane, propene, ethanol, acetone, and hexenal.

Oceans are a further natural source of NMVOC. Many studies on ocean emissions have been limited to light hydrocarbons. The estimation of 2.5-6 Tg yr^{-1} is based on this class only with the main compounds being ethane, propane, ethene, and propene (Warneck, 2000). There is uncertainty in the emissions of the heavier hydrocarbons. One study (Eichmann et al., 1980) suggested that global ocean emissions might be as high as

26 Tg yr^{-1}. Smaller scale studies though such as Duce et al. (1983) report results that suggest the emission rate could be a lot lower.

Soils can be either a sink or source of NMVOC, as some soil microorganisms emit NMVOC, but others can metabolize these compounds (Guenther et al., 2000). Warneck, (2000) suggests that the net flux is negligible for all compounds except ethane.

1.1.4.2. Biogenic NMVOC Production

Anaerobic decomposition of polymeric, monomeric, and oligomeric compounds (i.e. lipids, nucleic acids, polysaccharides, proteins, amino acids, glycerol, peptides, purines, pyrimidines and sugars) in animal waste, result in the formation of NMVOCs (Zahn et al., 1997). There is limited information relating the decomposition of specific polymeric, monomeric, and oligomeric compounds into particular classes of NMVOCs. Spoelstra (1980) reports that the deamination and decarboxylation of amino acids leads to the production of alcohols and ketones. In addition, it has been determined that volatile fatty acids are produced by anaerobic microbial fermentation of carbohydrates (Mackie et al., 1998) and aromatics such as 4-methylphenol by amino acid metabolism of tyrosine (Mackie et al., 1998; Spoelstra, 1980).

1.1.5. Environmental Impacts

1.1.5.1. RSCs

A potential environmental impact of RSC swine CAFO emissions is the effect of odor on the health of the local surrounding population who reside nearby. Chemical compounds are odorous when they exceed their odor detection threshold, which is

defined as the lowest concentration of a chemical compound that produces a sensory response in the olfactory receptors of humans (American Industrial Hygiene Association, (AIHA), 1989). In odor testing, it is defined as the minimum concentration of sensory response detected in 50% of the odor panel (AIHA, 1989).

Odorous compounds can cause health symptoms and health effects even if it is below an irritant threshold (Schiffman and Williams, 2005). This occurs because unpleasant odors can cause a change in the functioning of the human brain and body as a result of a biological response (i.e. the human nervous system reacts to bad odors to warn us against potentially unsafe air and food), which in turn can lead to the developments of health symptoms and health effects (Schiffman and Williams, 2005). RSCs are of particular concern as they have unpleasant odors and low odor thresholds. Table 1.3 shows the odor thresholds and characteristics of the five main RSCs ((hydrogen sulfide (H_2S), dimethyl sulfide (CH_3SCH_3), dimethyl disulfide (CH_3SSCH_3), carbon disulfide (CS_2), methyl mercaptan (CH_3SH)). It can be observed that all the RSCs have an odor threshold under 10ppb.

Schiffman and Williams (2005) identified six community studies where exposure to low concentrations of H_2S or RSCs have been related to health effects. In two of these studies, health effects were reported from an average daily H_2S concentration exposure of 10-11 ppb. There have also been a range of studies reporting human health effects associated with swine CAFOs. A study by Donham and Thu (1995) found 70% of workers at confined swine farms to have some kind of bronchitis, over 50% had upper airway inflammation and approximately 1 in 10 had asthma related symptoms. Wing and

Wolf (2000) using a rural community survey found that there were higher self-reported health symptoms in residents, who lived near swine farms. The residents were found to have increased occurrences of sore throat, runny nose, headaches, excessive coughing, burning eyes and diarrhea. In addition, the odor associated with swine CAFOs can also affect the quality of life for people living nearby. Wing and Wolf (2000) reported that people living near swine farms would not open their windows or go outside at certain times as a result of the odor.

RSCs can go through chemical reactions to form sulfur dioxide and then sulfuric acid (see section 1.1.6). Sulfuric acid deposition can have a number of detrimental environmental effects. In lakes, streams, and other water-bodies, sulfuric acid can reduce the pH level, killing a wide variety of biological species including fish, invertebrates, and microorganisms. Sulfuric acid can also damage tree and plant leaves, and root systems. Sulfuric acid deposition onto a leaf, erodes the cuticle wax, leading to injury to the leaf. In urban areas, sulfuric acid deposition can lead to erosion to buildings, structures and sculptures (Jacobson, 2002).

Sulfuric acid can also react and lead to the formation of ammonium sulfate. According to monitoring data, 47 % of $PM_{2.5}$ mass is ammonium sulfate in the eastern United States (EPA, 1995). The formation of particulate matter can impact human health, as the fine particles can penetrate and deposit deep within the human lungs (U.S. EPA, 1997a). These particles can also impair visibility (Seinfeld and Pandis, 1998). In addition to impairing visibility, the scattering of incoming solar radiation can also result in regional cooling (Lovelock et al., 1972).

1.1.5.2. NMVOCs

Certain NMVOCs are odorous, therefore they can cause odor-related health effects in the same way as RSCs (see section 1.1.5.1). The most complete survey of NMVOCs present at a swine CAFO was conducted by Schiffman et al. (2001). Of the 276 NMVOCs identified (excluding RSCs), 28 had an odor threshold below 10 ppb. The odor threshold and odor characteristic for these compounds are presented in Table 1.4.

A further potential effect of NMVOC is the formation of tropospheric ozone. In general NMVOC are highly reactive and through a set of reactions can form ozone (see section 1.1.7.). Ozone can affect human's respiratory system, leading to a reduction in lung capacity and increasing the potential development of asthma (Lippman, 1993).

In 1970, under the Clean Air Act, the EPA established primary National Ambient Air Quality Standards (NAAQS) for ozone amongst other pollutants. In order to 'protect human health with a adequate margin of safety, a daily 1- hour maximum standard of 120 ppb was established. In 1997, due to evidence that a longer averaging time might better represent the short-term effects of ozone exposure on the respiratory system, a daily 8-hour maximum concentration of 80 ppb was established (EPA, 1997b). As of March 2008, the EPA has reported that over 139 million people in the United States live in areas where the 8-hour standard is exceeded (EPA, 2008). Research has shown that there is a relationship between ozone and mortality below this standard (Bell et al., 2005; Bell et al., 2004). As a result, the EPA has revised the standard, reducing it to 75 ppb (EPA, 2008).

Another environmental impact is the formation of secondary organic aerosols (SOA) from NMVOCs. Organic aerosols contribute significantly to the total aerosol production in the USA. The EPA (2003) estimated that in the eastern United States, organic carbon contributes about 10-18% of aerosols; in the west, it is higher contributing as much as 25-40%. It has been suggested that organic aerosols have greater health effects than other types of aerosols (Baltensperger et al., 2008; Norwat et al., 2007) found an increased association between daily mortality and fine particulate matter in the summer, when secondary organic aerosol levels are typically higher.

Additionally, 162 out of 188 NMVOC that have been classified as hazardous air pollutants (HAPs). HAPs are defined as those pollutants that are known to cause cancer or other serious health effects such as damage to the immune system, reproductive, developmental, neurological, and respiratory effects (US EPA, 2009).

1.1.6. Reactions and Transport of RSCs

RSCs react readily with the hydroxyl radical (OH) species, which can result in the production of SO_2. SO_2 can be converted to sulfuric acid and particulate sulfate, resulting in the production of aerosols or acid deposition. The following is the chemical reactions for RSCs and how they can be converted to SO_2.

1.1.6.1. Hydrogen Sulfide (H_2S)

H_2S primary reaction in the atmosphere is likely to be with OH; the atmospheric lifetime of H_2S is ~ is 2-3 days (Seinfield and Pandis, 2006; Warneck, 2000).

$$OH + H_2S \rightarrow H_2O + HS \quad (7)$$

HS can then react to produce to SO or SO_2.

$$HS + O_2 \rightarrow OH + SO \quad (8)$$

$$\rightarrow SO_2 + H \quad (9)$$

HS can then have important reactions in the troposphere with NO_2 and O_3, and lead to the formation of SO_2.

$$HS + O_3 \rightarrow HSO + O_2 \quad (10)$$

$$\rightarrow OH + SO + O \quad (11)$$

$$HS + NO_2 \rightarrow HSO + NO \quad (12)$$

$$HSO + O_2 \rightarrow HO2 + SO \quad (13)$$

$$HSO_2 + O_2 \rightarrow SO_2 + HO_2 \quad (14)$$

$$SO + O_2 \rightarrow SO_2 + O \quad (15)$$

$$SO + O_3 \rightarrow SO_2 + O_2 \quad (16)$$

(Warneck, 2000)

1.1.6.2. Dimethyl Sulfide (CH_3SCH_3)

CH_3SCH_3 is the largest natural contributor to the global sulfur flux. Its main reaction is with the OH radical; it lifetime varies from 12 hours to just over 2 days (Seinfield and Pandis, 2006; Warneck, 2000).

$$OH + CH_3SCH_3 \rightarrow CH_3SCH_2 + H_2O \quad (17)$$

$$OH + CH_3SCH_3 + M \leftrightarrow CH_3S(OH)CH_3 + M \quad (18)$$

Reaction (17) is the abstraction path favored at higher temperatures; reaction (18) is the addition path, which is more likely to occur at lower temperatures.

The CH_3SCH_2 (reaction 17) radical behaves as an alkyl radical.

$$CH_3SCH_2 + O_2 + M \rightarrow CH_3SCH_2OO + M \quad (19)$$

$$CH_3SCH_2O_2 + NO \rightarrow CH_3SCH_2O + NO_2 \quad (20)$$

$$CH_3SCH_2O \rightarrow CH_3S + HCHO \quad (21)$$

Reaction (21) occurs quickly, so that the CH_3SCH_2O radical can be assumed to decompose immediately. When NO_x levels are low, $CH_3SCH_2O_2$ can react with the HO_2 radical. This can result in the formation of DMS.

$$CH_3SCH_2O_2 + HO_2 \rightarrow CH_3SCH_2OOH + O_2 \quad (22)$$

$$\rightarrow CH_3SCHO + H_2O + O_2 \quad (23)$$

$$CH_3SCHO + OH \rightarrow H_2O + CH_3 + COS \quad (24)$$

(Barnes et al., 1996)

The DMS-OH reaction produces COS as a minor production, yielding 0.7% S (Barnes et al. 1996). From reaction (18), $CH_3S(OH)CH_3$ can react to form dimethyl sulfoxide (DMSO), $CH_3S(O)CH_3$.

$$CH_3S(OH)CH_3 + O_2 \rightarrow CH_3SOCH_3 + HO_2 \quad (25)$$

By further oxidation, this can react to form CH_3SCH_3OO as $DMSO_2$.

From reaction (24), the product CH_3SO_2 can react to form Methanesulfonic acid (MSA), CH_3SOHOO or SO_2. The ratio of MSA to SO_2 is 0.1 near the equator and 0.4 in Antarctic water, indicating that MSA is favored in colder temperatures.

$$CH_3SO_2 \rightarrow CH_3 + SO_2 \quad (26)$$

$$CH_3SO_2 + O_3 \rightarrow CH_3SO_3 + O_2 \quad (27)$$

Dimethyl sulfide can also react with the nitrate radical, particularly at night, when there is no OH radical present.

$CH_3SCH_3 + NO_3 \rightarrow CH_3SCH_2 + HNO_3$ (28)

(Seinfeld & Pandis, 1998; Finlayson-Pitts & Pitts, 2000)

This can lead to CH_3S production by reactions 19-21. The overall mechanism for the fate of dimethyl sulfide is still not completely understood and there are still details of this mechanism that are uncertain (Seinfeld & Pandis, 1998).

1.1.6.3. Dimethyl Disulfide, (CH_3SSCH_3)

CH_3SSCH_3 has a significantly shorter lifetime than dimethyl sulfide of around 0.1 days (Warneck, 2000; Finalyson-Pitts and Pitts, 2000). As a result of its high reactivity, even small concentrations of dimethyl disulfide can affect the atmospheric environment significantly. As with dimethyl sulfide, it's main reaction is with the OH radical.

$OH + CH_3SSCH_3 \rightarrow CH_3SOHSCH_3$ (29)

$\rightarrow CH_3SOH + CH_3S$ (30)

(Finlayson-Pitts & Pitts, 2000)

As shown for dimethyl sulfide, CH_3S and CH_3SOH can then react to form SO_2 and MSA.

1.1.6.4. Methyl Mercaptan (CH_3SH)

CH_3SH also reacts by addition with the OH radical. Its typical atmospheric lifetime ranges from 0.3-0.4 days (Warneck, 2000; Finalyson-Pitts and Pitts, 2000).

$OH + CH_3SH \rightarrow (CH_3S(OH)H) \rightarrow CH_3S + H_2O$ (31)

It can also react with the nitrate radical to give a variety of products including CH_3SO_3H, SO_2, CH_3ONO_2, HCHO, CH_3SNO_2, HNO_3 and CH_3SSCH_3. Examples of the reaction are shown below.

$$NO_3 + CH_3SH \rightarrow CH_3S(NO_3)H \rightarrow CH_3S + HNO_3 \quad (32)$$

$$\rightarrow SO_2 + \text{other products} \quad (33)$$

(Finlayson-Pitts & Pitts, 2000)

1.1.6.5. Carbon Disulfide (CS_2)

CS_2 is estimated to have a reaction time of 7-7.2 days (Seinfield and Pandis, 2006; Warneck, 2000). Again like the other RSCs it reacts with the OH radical.

$$OH + CS_2 + M \leftrightarrow HOCS_2 + M. \quad (34)$$

Unless there is presence of O_2, the product will reverse to the original reactants. With the presence of O_2 a variety of products can be formed, with the main product being carbonyl sulfide (COS). In addition, CO can also be formed.

$$HOCS_2 + O_2 \rightarrow COS + HOSO \quad (35)$$

$$\rightarrow COS + H + SO_2 \quad (36)$$

$$\rightarrow COS + HSO_2 \quad (37)$$

$$\rightarrow COS + HO_2 + S \quad (38)$$

$$\rightarrow CO + HOSO + S \quad (39)$$

$$\rightarrow CO + H + SO_2 + S \quad (40)$$

(Finlayson-Pitts & Pitts, 2000)

1.1.6.6. Sulfur Dioxide (SO_2)

As discussed, RSCs react readily, and can produce SO_2. SO_2 can deposit through dry deposition or alternatively it can react to form sulfuric acid.

$$SO_2 + OH + M \rightarrow HOSO_2 + M \quad (41)$$

$$HOSO_2 + O_2 \rightarrow HO_2 + SO_3 \quad (42)$$

$$SO_3 + H_2O + M \rightarrow H_2SO_4 + M \quad (43)$$

(Seinfeld & Pandis, 1998)

Sulfuric acid can also lead to the formation of sulfate. It can condense due to its low saturation vapor pressure. Once condensed irreversibly, sulfuric acid dissociates reversibly.

$$H_2SO_4(g) \rightarrow H_2SO_4(aq) \leftrightarrow H^+ + HSO_4^- \leftrightarrow 2H^+ + SO_4 \quad (44)$$

Sulfuric acid can also react to form ammonium sulfate and ammonium bisulfate, depending on the type of atmosphere. In an extremely acidic atmosphere the aerosol particles will likely exist as H_2S solution. In moderate acidic atmospheric conditions, the particles will exist as bisulfate. In high ammonia concentration areas, ammonium sulfate will form (Seinfeld & Pandis, 1998).

$$NH_3 + H_2SO_4(aq) \rightarrow NH_4SO_4(aq) \quad (45a)$$

$$2NH_3 + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq) \quad (45b)$$

(Warneck, 2000)

Other factors that may effect this reaction include relative humidity and temperature (Seinfeld and Pandis, 2006).

1.1.7. Reaction and Transport of NMVOCs

In the troposphere, NMVOCs are highly reactive, and are most likely to react with the hydroxyl radical (OH), resulting in a typical lifetime on the order of hours. An example of a typical NMVOC degradation is shown below, where R and RH represent a organic group and a hydrocarbon, respectively.

$RH + OH \rightarrow H_2O + R\cdot$ (46)

$R + O_2 + M \rightarrow RO_2\cdot + M$ (M=air) (47)

$RO_2 + NO \rightarrow RO\cdot + NO_2$ (48)

$RO\cdot + O_2 \rightarrow$ Oxidated Hydrocarbon$+ HO_2$ (49)

$HO_2 + NO \rightarrow OH + NO_2$ (50)

(Atkinson, 2000)

These reactions show the creation of the $RO_2\cdot$ and HO_2 radicals, which shown in equations (48) and (50) react with NO, converting NO to NO_2. From here, O_3 is formed from the photolysis of NO_2

$NO_2 + h\nu \rightarrow NO + O(^3P)$ (51)

$O(^3P) + O_2 + M \rightarrow O_3 + M$ (M= an inert gaseous specie e.g. nitrogen gas) (52)

(Atkinson, 2000)

The RO_2 radical can also react with the HO_2 radical, which does not lead to the formation of O_3. The competition between RO_2 reaction with either NO or HO_2 is very important in determining O_3 formation, and individual NMVOC react in different ways (Atkinson, 2000). Additionally during the nighttime, RO_2 can react with NO_3 radical to form NO_2.

$$RO_2 + NO_3 \rightarrow RO + NO_2 + O_2 \quad (53)$$

NMVOC can also form secondary organic aerosols (SOA). For an aerosol to form, a reaction product must be formed in the gas phase at a concentration equal to its saturation concentration. This will not occur if the vapor pressure of the reaction product is higher than the initial concentration or if the gas phase reactions of the NMVOC are too slow (Grosjean, 1992). As a result of high vapor pressures, many NMVOC do not form aerosols, regardless of their gas-phase reactivity. It has been concluded that only NMVOC containing seven or greater carbon atoms can form SOA (Odum and Jungkamp, 1997).

There are very limited studies in the formation of SOA from alkane photooxidation. Wang et al. (1992) reported a 9% average aerosol yield by mass for methylcyclohexane. There have been numerous studies of alkenes, mainly due to the large amount of alkenes produced by vegetation. Pandis et al. (1991) examined a range of alkenes and found the aerosol yield to vary greatly for each specie. Isoprene had a negligible aerosol yield, α-pinene approximately 3%. More significantly, the biogenic compound β-pinene had an aerosol yield of 30-40%. The highest yield was for trans-caryophyllene, which had ~100% aerosol yield.

Odum et al. (1997) studied the potential for SOA formation from gasoline vapor, which emits compounds from a wide range of chemical groups. Using an outdoor smog chamber, the researchers concluded that aromatics dominate SOA formation in urban areas.

1.1.8. H_2S Emissions from Swine CAFOs

There have been many studies of H_2S emissions from swine CAFOs in the Midwest of the U.S. This includes measurements of barn emissions from a range of swine management systems (Heber et al., 1997; Ni et al., 2002; Zhu et al., 2000; Jacobson et al., 2003; Jacobson et al., 2004; Heber et al., 2004) and measurements of lagoon emissions (Zahn et al., 2001, Lim et al., 2003, Byler et al., 2004). However, North Carolina swine CAFO emissions have not been studied as extensively. Blunden et al. (2008) and Blunden and Aneja (2008) are the only known studies that have measured lagoon and barn H_2S emissions from a swine CAFO in North Carolina. Details on previous studies' measurements of lagoon fluxes and barn concentrations and emissions are presented in Table 1.5 and Table 1.6, respectively.

It can be observed that lagoon fluxes range from ~0 to 1266 $\mu g\ m^{-2}\ min^{-1}$ (Blunden and Aneja, 2000; Zahn et al., 2001), barn concentrations from 8.7-632 ppb (Jacobson et al., 2003; Blunden et al., 2008) and barn emissions from 0.11 – 8.5 $g\ day^{-1}\ AU^{-1}$ (AU represents 1 animal unit, which is equal to 500 kg of live animal weight). The variance in the magnitude of lagoon fluxes, and barn concentrations and emissions is due to differences in environmental, production and management conditions. It is noted that H_2S barn concentrations are significantly above their odor thresholds.

1.1.9. RSC Emissions from Swine CAFOs

In comparison to H_2S, other RSCs have not been studied as extensively. Currently, less than a handful of studies (Clanton and Schmidt, 2000; Blunden et al.,

2005; Kim et al., 2007; Trabue et al., 2008a) have reported concentrations of other RSCs at swine facilities. Of these studies, none have reported lagoon fluxes and only one has reported barn emission rates, which was conducted in South Korea (Kim et al., 2007). Details of the previously reported RSC concentrations are provided in Table 1.7. It can be observed that CH_3SH concentrations range from 0-16 ppb, DMS concentrations from 0-8.4 ppb, CS_2 from 2.4-45ppb and DMDS concentrations from 0-4.7 ppb. This suggests that RSCs concentrations may exceed their odor threshold. It should also be noted that Schiffman et al., (2001) identified 30 sulfur compounds from a swine CAFO in North Carolina, which included H_2S, DMS, DMDS, CH_3SH and CS_2.

As mentioned, the Kim et al. (2007) study also reported RSC barn emission rates. The emission rates from the five different facility types ranged from 0.43-1.92 g day^{-1} AU^{-1} for CH_3SH, 0.20-0.93 g day^{-1} AU^{-1} for DMS and 0.12-0.58 g day^{-1} AU^{-1} for DMDS.

1.1.10. NMVOC Emissions from Swine CAFOs

Similarly to RSCs, there have been limited measurements of NMVOCs from swine CAFOs. Studies include reports of barn concentrations (Blunden et al., 2005; Trabue et al., 2008b), concentrations from a deep basin waste storage system (Zahn et al. 1997) and identification of compounds present in anaerobic lagoon water and barn air (Schiffman et al., 2001). Currently, there is no known study that has reported NMVOC emissions from swine CAFOs with respect to seasonal and environmental variations.

Schiffman et al. (2001) identified 276 NMVOCs (excluding RSCs) in the air from a swine barn in North Carolina. Of the 276 NMVOCs, 27 were odorous NMVOCs (i.e

they have an odor threshold less than 10 ppb), and 22 were HAPs. The odorous compounds are presented in Table 1.4 and the HAPs in Table 1.8. In addition, Table 1.8 indicates other swine CAFO studies that have also identified these HAPs. Of the 27 'low odor threshold' compounds, concentrations were reported for 12 of them, with 5 exceeding their odor threshold. These were butanoic acid, 3-methylbutanoic, 2-methylbutanoic acid, 4-methylphenol, and indole. It should be noted that three compounds 2-methylphenol (o-Cresol), 3-methylphenol (m-Cresol) and 4-methylphenol (p-Cresol) are odorous and are also defined as a HAP.

Zahn et al. (1997) identified 24 NMVOCs in the air above a deep basin waste storage system, including four odorous compounds. These were butanoic acid, pentanoic acid, phenol and 4-methylphenol. 4-methylphenol was found to exceed its odor threshold. In addition, 3 HAPs were identified, phenol, 4-methylphenol and 3-methylphenol.

In a more recent study, Trabue et al. (2008b) measured 11 NMVOCs concentrations in a swine finishing barn in Iowa. They identified five compounds to be exceeding their odor thresholds: butanoic acid, 4-methylphenol, 4-ethylphenol, indole, and 3-methylindole. Two HAPs were also identified (4-methylphenol and phenol).

Blunden et al. (2005) made measurements of NMVOC concentrations from swine barns in North Carolina. Measurements were made in two different seasons at both a mechanically ventilated and a naturally ventilated barn in North Carolina. Concentrations were reported for the odorous compound, 4-methylphenol. For one season at both swine CAFOs, 4-methylphenol exceeded it's odor threshold. In addition, 4-methylphenol is also a HAP. Blunden et al. (2005) also reported a second HAP, methanol.

1.2. METHOD AND MATERIALS

1.2.1. Sampling Site

The sampling site (Figure 1.4) is a commercial swine CAFO located in eastern North Carolina, in Jones County. At the swine CAFO, there are eight finishing barns with between 900-1000 pigs in each barn. Generally, the pigs weigh between 20-24 kg on arrival, and stay at the barn for 16-20 weeks. The barns are mechanically ventilated.

The swine farm uses a conventional waste management method, known as 'Lagoon and Spray Technology'. In this method, the swine waste falls through slatted floors into a shallow manure collection pit. The swine waste is then flushed weekly from the shallow pit through pipes into an anaerobic treatment lagoon. Periodically, the anaerobic treatment lagoon waste is sprayed over crop fields for nutrient enrichment. The anaerobic treatment lagoon liquid is also used to flush the barn manure pits. This waste management method is used by the majority of swine CAFOs in North Carolina.

1.2.2. Sampling Scheme

Measurements of emissions were made during all four seasonal periods during 2007-2008. Emissions from both the lagoon and barn were each measured for a ~ 1week period during the sampling seasons. Sampling was conducted during the summer season from June 8th-June 28th, 2007; the fall season from the October 20th -November 12th, 2007; the winter season from February 8th-February 29th, 2008; and the spring season from 11th April-April 28th, 2008. RSCs and NMVOC emissions were measured using two

different analytical techniques. Continuous H_2S measurements were made in-situ by a pulsed fluorescence H_2S analyzer. The NMVOCs and the other RSCs were collected using passivated canisters and analyzed ex-situ by a GC-FID.

1.2.3. Field Sampling Technique

1.2.3.1. H_2S

A thermo environmental instrument (TEI) model 450C pulsed fluorescence H_2S/SO_2 analyzer (Thermo Environmental Corporation, Mountain View, CA) was used to continuously measure H_2S concentrations. The H_2S/SO_2 analyzer has a range of 0-1000 ppb. Before each sampling period, a multi-point calibration was conducted on the analyzer. This was performed using a TEI model 146 dilution-titration system (Thermo Environmental Corporation, Mountain View, CA). Additionally, zero and span checks were conducted regularly during the sampling periods. These were also performed after each sampling period. It should be noted that SO_2 concentrations were not analyzed at the swine CAFO, as concentrations were negligible.

1.2.3.2. RSCs and NMVOCs

1.2.3.2.1. Stability of RSCs and NMVOCs

Field sampling of RSCs (excluding H_2S) and NMVOCs was conducted by collecting whole air samples. The whole air samples were collected using 6-L passivated canisters. Both SUMMA and fused-silica lined (FSL) canisters were used for sampling.

The SUMMA canister has an interior surface made of stainless steel, which is passivated by electrolysis and coated with a chrome-nickel oxide layer (Hsu et al., 2001).

Humidified SUMMA canisters have been shown to be stable for a wide range of non methane volatile organic compounds (NMVOCs) for up to four weeks (Brymer et al., 1996; Ochiai et al., 2002). However, humidified SUMMA canisters are reported to be unsuitable for mercaptans (Brymer et al., 1996; Ochiai et al., 2002) including the sulfur compound of interest CH_3SH (Brymer et al., 1996). The stability of the other sulfur compounds of interest, DMS and DMDS, in humidified SUMMA canisters is uncertain, as there has been no known peer-reviewed study investigating the stability of these compounds.

FSL canisters are constructed of stainless steel in which a fused-silca coating has been added to the interior of the canister. Similarly, humidified FSL canisters are stable for a wide range of NMVOCs for up to four weeks (Ochiai et al., 2002). However, the fused-silca coating is applied to improve the recovery of RSCs. A recent study reported DMS and DMDS to have good recovery in humidified FSL canisters (Trabue et al., 2008a). This study also found that CH_3SH had poor recovery in humidified FSL canisters. However, CH_3SH had good recovery in dry FSL canisters.

1.2.3.2.2. Canister Sampling Scheme

Nine to eleven canister samples were taken from both the lagoon and barn over each measurement period. A mixture of 6-L SUMMA and FSL canisters were used for sampling. Of these, approximately a quarter were FSL canisters. Prior to sampling, the canisters were cleaned by a XonTech Model 960 canister cleaning system. The automated system performs a cycle of cleaning, where canisters are evacuated, filled with

humidified air and then baked at 120^{o}C. The canisters were cleaned using 2 cycles. After the cleaning, the system evacuates the canisters to < 0.05 mm Hg using a vacuum pump.

Samples were taken over a period of 5 minutes at different times of the day (between 8:00 and 18:00 EST) and in different meteorological conditions to examine the factors that influence RSCs emissions. Canister samples from the lagoon and barn were collected from a minimum of four different days over each sampling period.

1.2.4. Flux Measurements

1.2.4.1. Lagoon Measurements

Anaerobic treatment lagoon flux was determined using a dynamic flow-through chamber system (Blunden and Aneja, 2008; Aneja et al., 2000). A schematic and photograph of the chamber system are presented in Figures 1.5 and 1.6, respectively. The chamber is a cylindrical shape, with an internal height and diameter of 46 cm and 26 cm, respectively. This results in a total volume of the chamber of ~ 25.4 liters (L). A closed system is formed, as ~7cm of the bottom of the chamber protrudes into the lagoon forming a seal.

The inside of the chamber is lined with ~0.05mm thick fluorinated ethylene propylene (FEP) Teflon. The chamber sits inside a circular hole in a 0.61m x 0.61m floating platform, which is composed of ultra-high molecular weight (UHMW) polyethylene, with a thickness of 1.27 cm. Attached to either side of the platform are two PVC pipes (diameter 15.24 cm, length 168 cm), which provide additional buoyancy.

Into the chamber through Teflon tubing (0.64 cm outer diameter, 0.4 cm inner diameter) flows compressed zero-grade air (Machine and Welding Supply Company, Raleigh, NC) at a flow rate of ~ 4 L min^{-1}. This flow rate is controlled/set by a Model 810–S Mass Trak Flow Controller (Sierra Instruments, Monterey, CA). A variable-speed motor rotates a Teflon impeller inside the chamber at speeds of 40-60 rpm. This ensures that the air is well mixed similarly to ambient air. The out flowing air flows through more Teflon tubing into the H_2S/SO_2 analyzer or passivated canister. The out flowing part of the system has a vent. Any air that is not required exits this vent. Additionally, the vent ensures that the closed system does not become over pressurized. The vent was bubble tested to check for leaks and under pressurization. The fittings used in the system were all made of stainless steel, in order to minimize chemical reactions.

1.2.4.2. Lagoon Flux Calculation

In order to calculate the lagoon flux, the following mass balance equation is used.

$$\frac{dC}{dt} = \left(\frac{qC_o}{V} + \frac{JA}{V}\right) - \left(\frac{L_T A_w}{V} + \frac{q}{V}\right)[C] \qquad (54)$$

where, q is the flow rate of carrier gas through chamber, C_o is the concentration of the compound in the carrier gas, J is the compound flux, A is the cross sectional area of the top and bottom of the chamber, V is the volume of chamber above the lagoon surface, L_T is the loss term, which is the total loss of a compound in the chamber due to reaction with the inner and upper walls of the chamber, A_w is the surface area of inner and upper walls of the internal chamber, C is the concentration of the compound within the chamber.

As mentioned, zero-grade air is used for the carrier gas, therefore $C_o = 0$. Additionally, when the system reaches steady state, the instantaneous change of concentration with time approaches zero, therefore dC/dt = 0. Therefore equation (54) is simplified to the following:

$$J = [C\ ]\left[\frac{L_T A_w}{V} + \frac{q}{V}\right]h \quad (55)$$

where h is the height of the chamber.

1.2.5. Barn Measurements

Barn measurements were made at one of the eight swine barns at the sampling site. At the west end of the barn facing the lagoon there are five ventilation fans (AAA.Associates Inc. Maxi-Brute™ fans, Niles, MI). All five fans had plastic shutters. Three are belt driven with a diameter of 122 cm. Two of the fans are direct driven, and have a diameter of 91 cm. The fans turn on in a set sequence, as barn temperature increases. The barn flow rate was calculated using the following equation:

$$Calculated\ fan\ flow\ rate = Manufactures\ fan\ flow\ rate \times \left(\frac{Measured\ RPM}{Specified\ RPM}\right) \quad (56)$$

The measured revolutions per minute (RPM) were determined using a rotation-voltage relationship system (Blunden et al., 2008). Measured revolutions per minute (rpm) were calculated by attaching Mabuchi VDC motors (Santa Clara, CA) to the fans. For the direct driven fan's, the motor was mounted to a stainless plate, which lies over the fan's original plate. For the belt driven fan's, a cylinder sleeve was placed over the fan shaft. From the motors, single analog output wires were used to connect each motor to a

data logger (Campbell Scientific CR10X, Logan, UT). Therefore if a fan was rotating, a voltage was recorded. To determine the relationship between voltage and rpm, the motors were calibrated before the beginning of the field campaign using a Dayton SCR controlled DC Motor (Model # 2M168C). The motors were attached to the shaft of the controlled DC motor. From this, simultaneous rpm and voltage were measured using a Shimpo DT-207B Direct Contact Digital Tachometer, a Shimpo DT-725 stroboscopic Digital Tachometer, (Itasca, IL) and a Micronta Digital Multimeter (Model # 22-185). From this procedure a calibration curve was determined. For every sampling season, the stroboscopic tachometer was used to check and evaluate each fan's performance. From this, the calibration curve was adjusted accordingly for each season.

The manufactures specifications are 850 rpm for the direct drive motors and 1725 rpm for the belt driven motors. However it has been estimated that the pulley ratio is approximately 2:9:1, resulting in the fans rotating at approximately 595 rpm.

Measurements of the static pressure difference were made between the inside and outside of the barn using a hand held pressure sensor. Pressure readings were taken daily during all the sampling seasons. When taking readings, it was noted how many fans were on. These measurements were used to determine the average static pressure difference, when a certain number of fans were on. The manufacturers fan flow rate was adjusted accordingly for the average static pressure difference.

Barn concentration measurements were made by placing a sample line made of Teflon tubing (0.64 cm outer diameter, 0.4 cm inner diameter) directly in front of the first fan to turn on. The concentration distribution across the fan was assumed to be uniform.

Concentrations were assumed to be equal for all barn fans. Background barn samples were collected upwind of the barns using fused-silca lined canisters. Concentrations in background samples were negligible in comparison to the corresponding H_2S concentration from the barn fan, therefore they are not considered in emission calculations. For other RSCs and NMVOCs, background canister samples were taken simultaneously to the barn samples. The samples were collected upwind of the swine house, and were analyzed identically to the barn canister samples. Net sample concentrations were calculated for each compound. However, it should be noted that no RSCs were identified in background samples.

The barn emission rates were calculated using the following equation:

$$J = C * \sum f \qquad (57)$$

where J is the compound flux, C is the gas concentration at the fan, $\sum f$ is the sum of the flow rates of each individual fan.

1.2.6. Environmental Parameter Measurements

During lagoon sampling, lagoon temperature and lagoon pH were measured continuously. Lagoon temperature was measured by a CS107 temperature probe (Campbell Scientific Inc., Logan, UT). A model CSIM11 pH probe (Campbell Scientific Inc., Logan, UT) was used to measure lagoon pH. The pH probe is placed in buffer solution and calibrated before and after each sampling period of ~ 1 week. Both

probes are submerged ~7cm below the lagoon surface. For barn sampling, a CS107 temperature probe was used to measure temperature at the fan outlet.

Near-surface (< 10 cm) anaerobic treatment lagoon samples were taken daily to be analyzed for sulfide content. The lagoon samples were preserved for sulfide analysis by adding 1ml of 2N zinc acetate and ~6N NaOH until the pH>9. The samples were stored below 4^{o}C until analysis. Samples were analyzed within 5 days of collection at the North Carolina Division of Water Quality. Sulfide content was measured by color metric analysis. This was performed using Standard Method 4500-S2-D (Greenberg et al., 1999).

A Model CR23X Data logger model and a CR10X Data logger, which has a Model AM 16/32 Channel Relay Multiplexer (Campbell Scientific Inc., Logan, UT) were used to record and collect all data. The data was downloaded to a laptop daily. The datalogger and the H_2S/SO_2 analyzer were housed inside a mobile laboratory (NC State University Air Quality Ford Aerostar Mini-Van). To ensure that the instruments worked efficiently, the temperature inside the mobile laboratory was maintained to room temperature at ~ 21^{o}C.

1.2.7. Instrumentation/Theory of instrumentation

1.2.7.1. TEI Model 450C Hydrogen Sulfide Analyzer

1.2.7.1.1. Theory of Operation

The Thermo Environmental Instruments (TEI) model 450C hydrogen sulfide analyzer is based at the theory that H_2S can be converted into SO_2. Then the converted

SO_2 molecules absorb ultraviolet light, resulting in their excitement at a particular wavelength. This will result in decay to a lower energy state, thus the UV light is emitted at a different wavelength. This process is described by the following chemical reactions.

$$H_2S^* \rightarrow SO_2 \quad (58)$$

$$SO_2 + hv_1 \rightarrow SO^*_2 + hv_2 \quad (59)$$

The detection process is started with the sample being drawn into the model 450C through the sample bulkhead. Next the sample can go in two ways. The sample can pass through the converter and H_2S levels can be inferred, or the sample can bypass the converter and go to a hydrocarbon kicker. In order for SO_2 concentrations to be determined, the sample flows to the hydrocarbon kicker. The kicker removes hydrocarbons by forcing the hydrocarbon molecules to differentially permeate through a tube wall. Conversely, the SO_2 molecules can pass through the hydrogen kicker without being affected.

The next stage of the process is the flow of the sample into a fluorescence chamber. Here there is a pulsating UV light that excites the SO_2 molecules. This emitted light is focused by mirrors that only reflect the wavelengths that excite SO_2 molecules. As the excited SO_2 molecules decay to their lower energy states, they release light. This light is proportional to SO_2 concentration. The light passes through a filter that only allows the wavelengths released by the excited SO_2 molecules to pass through and thus be detected by a photo multiplier tube (PMT). The detector continuously monitors the pulsating UV light source. If there are any fluctuations in the UV light, there is electronic

circuitry, which is connected to the detector, which will compensate for these fluctuations.

Finally the sample flows through a flow sensor, and a capillary, before entering and leaving the shell side of the hydrocarbon kicker. The model 450C outputs the $SO_2/H_2S/CS$ (complete sulfur = SO_2 +H_2S) and the analog outputs to the front panel display. A schematic of the 450C is presented in Figure 1.7 (Obtained from TEI, 2002).

The H_2S/SO_2 analyzer averages concentrations every minute, and has a maximum detection limit of 1000 ppb.

1.2.7.1.2. Calibration

A multi-point calibration was conducted for the TEI Model 450C H_2S/SO_2 analyzer before each experimental period. This was achieved by using cylinders of 29 ppm and 500 ppb of H_2S, and 10.9 ppm of SO_2 (Machine and Welding gases, NIST certified). These gas cylinders were diluted for calibration using a TEI Model 146 dilution-titration system.

1.2.7.2. GC-FID

Past studies have indicated that concentrations of NMVOC and RSCs (excluding H_2S) are typically in the sub-20ppb range and can be less than 1ppb. Therefore to detect a range of compounds with a sensitivity of less than 1ppb, a gas chromatography- flame ionization detection (GC-FID) system was used. A flame ionized detector (FID) detects compounds with a hydrocarbon bond, which includes the majority of NMVOCs and the RSCs of interest dimethyl sulfide (DMS; CH_3SCH_3), dimethyl disulfide (DMDS; $CH_3S_2CH_3$) and methyl mercaptan (CH_3SH).

1.2.7.2.1. Analytical System

Analysis of the canisters was conducted at the National Exposure and Research Laboratory (NERL) of the US Environmental Protection Agency (EPA) in Research Triangle Park, NC. Samples were analyzed using a Hewlett-Packard Model 5890A (Avondale, CA) gas chromatography system. The system includes a cryogenic u-shaped stainless steel trap, which is used to pre-concentrate the sample using liquid argon (-187^{o}C). The sample is drawn onto the cryogenic trap, which is immersed in liquid argon, the trap is then immersed in a dewar of boiling water (~99^{o}C). The sample is then separated using a J & W Scientific (Folsom, CA) DB-1 column (60m x 0.32mm x 1 μm). Helium carrier gas is kept at a constant pressure of 150kPA. At 75^{o}C, this provides a flow rate of 2.65 cm^3 min^{-1}. The initial column temperature is -50^{o}C, this temperature is held for two minutes, and then increases at a rate of 8^{o}C/min to 200^{o}C. The temperature is then held at 200^{o}C for 7.75 min, before a further temperature increase of 25^{o}C/min to 225^{o}C. Finally the temperature is held at 225^{o}C for 8 minutes. The FID applies a voltage of 200v and was maintained at a temperature of 275^{o}C. The flow rates for hydrogen and air were 48 and 325 cm^3 min^{-1}, respectively, with a make-up gas of 30cm^3 min^{-1} of nitrogen.

The data integration system is performed using the ChromPerfect-5890 Direct chromatographic software program (Justice Innovations, Mountain View, CA). A different software program known as HCID (Graham Solutions, Conyers, GA) is used to check the integration, and manually re-integrate as necessary. This software also allows the use of a file named CALTABLE, which contains approximately 300 compounds

retention times, retention index and compound name including the RSCs, DMS, DMDS and CH_3SH.

The GC-FID detects in ppbC (parts per billion carbon), therefore to convert from ppbC to ppb, a compound is adjusted using it's effective carbon number (Scanlon and Willis, 1985; Kallai and Balla, 2002; Jorgensen et al., 1990). The limited information available suggests that sulfur has no effect on FID response (Jorgensen et al., 1990).

1.2.7.2.2. Calibration

Calibration of the GC-FID system was performed using 0.25 ppm ± 1.2% propane in air (National Institute of Standards and Technology Standard Reference Material). From the slope of the multi-point calibration curve, a response factor is determined based on ppbC area^{-1}. This is applied to all observed peaks. The FID has a uniform carbon response for all peaks, therefore a single response factor can be used to represent all compounds (Blades, 1976; Sternberg et al., 1962). Additionally a 4 compound standard cylinder containing Ethane (48.7ppb), Propane (53.9 ppbC), Isobutane (51.2ppb), and n-Butane (54.6 ppbC) is used regularly to provide verification of retention time location, and FID response. For quality assurance and quality control, the analytical reproducibility is tested by repeat analysis of samples.

In order to confirm the accuracy of the peak naming procedure or to identify unknown compound peaks a gas chromatography-mass spectrometry (GC/MS) system is used. The analytical instruments are a Hewlett-Packard Gas Chromatograph Model 6890 combined with a Hewlett Packard Model 5972 Mass Selective Detector. The same column, temperature program, and pre-concentration system is used for the GC-MS as

the GC-FID. A difference between the systems is the use of an electronic pressure control device to keep the helium carrier flow rate constant at 1.4 cm^3 min^{-1}, throughout the temperature program. This occurs due to pressure changing with column temperature. At 75^oC, the pressure is measured as 67 kPa.

1.2.7.2.3. Theory of Operation

The official definition of chromatography is 'a physical method of separation in which the components to be separated are distributed between two phases, one of which is stationary (stationary phase) while the other (the mobile phase) moves in a definite direction' (IUPAC, 1974). In this study, the mobile phase is the carrier gas, and the stationary phase is a column.

In order to conduct the scientific methodology known as gas chromatography, a Hewlett-Packard Model 5890A is used. The main components of a GC are the carrier gas, the column and the detector.

1.2.7.2.3.1. Carrier Gas

There are two main properties that effect the selection of a gas for the mobile phase, non-reactivity and cost. Therefore there are three main carrier gases, N_2, He, and H_2. The choice of carrier gas is important, as it can affect resolution through its effects on column efficiency. This occurs as a result of the differences in diffusion rates for various gases. Figure 1.8 is a typical example of a van Deemter curve, and how the carrier gases can affect column efficiency. The smaller the Height Equivalent To one Plate (H.E.T.P), the more efficient the column. The van Deemter curve shows how nitrogen is more

efficient at an average linear velocity ~ 10 cm s^{-1}, but Helium and Hydrogen are more efficient over a wider range of linear velocities.

Helium is the carrier gas used in this system, as a result of the aforementioned wide range of efficiency. It is also cheap and safe. The column head pressure is kept constant throughout the temperature program by the use of an electronic pressure control device. The electronic pressure control device, keeps the helium carrier gas at a constant pressure of 150 KPa, allowing the carrier gas flow rate to vary with temperature. It is measured that the 150kPa pressure provides a carrier gas flow rate of 2.65cm^3 min^{-1} at 75^oC. Using the column information given below, this produces a linear velocity of 33cms^{-1}, for this flow rate, which is in the middle of the high efficiency part of the curve (Figure 1.8).

1.2.7.2.3.2. Column

A column is used to separate the gas compounds in the sample. Each compound has an individual retention time. The retention time is the time needed for the compound of interest to move from the point of introduction into the system to the point of detection. The mechanism of retention in a column is explained by the plate theory (Martin and Synge, 1941). The plate theory is based on the assumption that the solute/compound is at all times in equilibrium between the two phases. This occurs as a result of a continuous exchange of the compound between the mobile and stationary phases as it travels through the column. The smaller the plates in the column, the more efficient the exchange. Smaller plates also result in an increased number of plates, increasing what is known as column efficiency.

There are two main factors that influence retention time. The first is the time it takes a compound to travel through space occupied by the mobile phase. This is also known as dead space or dead time, and this is a characteristic that equally effects the retention time of all compounds. The second factor is the time the compound spends retained in the column, which depends on a range of characteristics.

An important factor in influencing the retention of the solute is the polarity of the stationary phase. For a column to be at its most efficient, it needs to have a polarity similar to the compounds of interest. Polarity is determined by intermolecular forces. Intermolecular forces can be classified as van der Waals forces. These are classified into three types, dispersion, induction, and orientation. There are various ways in which the interaction between the solute and the column are mathematically explained. These include the separation factor, Kovats retention index, the Rohrschneider-McReynolds constants and the activity co-efficient (McNair and Miller, 1998).

Columns are sub-divided into two main types, pack columns and capillary columns. In a pack column, the stationary liquid phase is coated on a solid support. For most effectiveness, the solid support or packing material is chosen for its surface area and inertness (Mc Nair and Miller, 1998). Capillary columns are open tubes, which are usually coated with a thin film of liquid phase. The column used in this experiment is a J & W Scientific (Folsom, CA), DB-1. It is a fused silica capillary column of 60m in length, and has an inner diameter (ID) 0.32 mm. The column has a 1 micron DB-1 coating. The column is bonded and cross linked, and is described as non-polar and has a maximum temperature limit of 325^{o}C (Agilent, 2007).

1.2.7.2.3.3. Temperature

The use of temperature in gas chromatography is one of the most important components of the analysis. This is a result of the relationship between temperature and vapor pressure, which is described by the Clausius-Clapeyron equation.

$$\log p^0 = -\frac{\Delta H}{2.3\,RT} + c \qquad (60)$$

ΔH = enthalpy of vaporization at absolute temperature, T
p^0 = compound's vapor pressure at this temperature
R = gas constant
c = constant (McNair and Miller, 1998)

Therefore, it can be inferred that an increase in temperature will increase the vapor pressure of the solute logarithmically. An increase in vapor pressure increases the amount of solute in the mobile phase. Other effects of an increase in temperature include a decrease in the retention time and a decrease in the retention volume.

The retention time of individual compounds is influenced by their boiling point and vapor pressure, but generally with NMVOC, the greater the carbon number, the higher the boiling point and the lower the vapor pressure. As a result of the diversity of NMVOC physical properties, a temperature ramp is needed. Temperature ramps vary depending on the needs of the research. A temperature ramp can be used to decrease retention volume (increase detection limits), improve separation, produce better peak shapes and improve precision. Potential problems of a temperature ramp include an increasing baseline due to column bleed, and an increase in time between samples due to

column cool down. To optimize the separation of NMVOC and RSCs, the column initial temperature is -50^{o}C. The temperature is held for two minutes, and then increased at a rate of 8^{o}C/min to 200^{o}C. The temperature is then held at 200^{o}C for 7.75 min, before a further temperature increase of 25^{o}C/min to 225^{o}C. Finally the temperature is held at 225^{o}C for 8 minutes. NMVOC with high boiling points range from 200-225^{o}C. The initial ramp of 8^{o}C per minute ensures that there is good separation of the NMVOC.

1.2.7.2.3.4. Flame Ionized Detector (FID)

For the analysis of NMVOC at low ppb levels, the most suitable detector is the Flame Ionized Detector (FID). The FID works by directing the output from the column into a hydrogen flame. A voltage of 200v is applied between the hydrogen flame and a stainless steel electrode, which is located away from the flame. The flame burns the carbon particles, which emit electrons. The emitted electrons increase the current, which is measured. There are two important factors in the optimization of the flame, the hydrogen and air flow rates and the carrier flow rate into the detector. For this system the optimized flow rates for hydrogen and air were 48 and 325 cc/min, respectively. Due to the size of the ID of the column, the carrier flow rate is below the optimum needed for the FID. Therefore a make-up gas was of 30cc/min of nitrogen was added to the total gas flow into the FID. The flame is heated and maintained at a temperature of 275^{o}C.

1.2.7.2.3.5. Pre-concentration

Pre-concentration is a name for a system that increases the ratio of trace constituents, thus increasing the sensitivity of the GC-system. When collecting samples in the ambient air, there are extremely high levels of nitrogen and oxygen. To remove

these from the sample to avoid interference, a cryogenic trap is used. 60-80 mesh untreated glass beads are packed inside a u-shaped stainless steel trap. The dimensions of this trap are 25 cm x 3.2 mm. The sample flows through the trap, which is immersed in liquid argon at a temperature of -187^{o}C. Due to their higher boiling point, the trace compounds of interest, i.e. NMVOCs condense onto the unreactive surfaces of the glass beads. As a result of their low boiling temperatures nitrogen and oxygen do not condense and pass through the trap as a gas. These trapped compounds are latter volatized by immersing the trap in boiling water (~99^{o}C), before being swept into the detector by the carrier gas.

1.2.7.2.3.6. GC-FID System

The GC system is composed of a variety of parts that come together to form the complete analytical instrument. A key part of the system is a 6 port rotor-type valve (Valco, Conical, Houston, TX), which is used in two different settings. The valve connects the various components of the system, and controls the appropriate flow system needed for the process of gas chromatography. Additionally in the GC-system are a ballast tank of 1.8 liter volume, a diaphragm pump (Thomas Model 2107VA20A, Sheboygan, WI) and a vacuum gauge (Wallace and Tieran Model 61D-1D-0200, Belleville, NJ). The GC-FID analysis is composed of 5 stages. Stages 1-5 are shown in figures 1.9 a,b,c,d, and e, respectively.

1.Using a vacuum pump a ballast tank is evacuated to a pressure of ~ 40 mm Hg mm, and the trap is immersed in a Dewar of liquid argon (-187^{o}C). The 6 port valve is in ‘trap’ mode. The helium carrier gas is flowing directly into the column.

2. When the trap has reached temperature equilibrium, the 6 port valve is switched to 'inject' mode, the canister valve is opened and the flow path to the ballast tank is opened. This allows the sample to be drawn by the pressure differential into the ballast tank.

3. When the pressure gauge on the ballast tank reaches 80 mm Hg, the 6 port valve is switched to 'trap' mode, and the sample from the canister is drawn onto the cryogenic trap at a flow rate of ~120cc/min. As the sample is drawn into the ballast tank, the NMVOC and RSCs condense onto the cryogenic trap.

4. When the ballast tank pressure reaches 140 mm Hg, the canister valve and ballast tank valve are closed. Next the 6 port valve is switched back to 'inject' mode, and immediately the Dewar of liquid argon is quickly replaced by a Dewar of boiling water (~99^{o}C), volatizing the NMVOC and RSCs, which are swept into the column to be separated.

5. After 2.25 minutes, which is long enough for all the NMVOC and RSCs to be swept onto the column plus 0.5 minute of leeway time, the 6 port valve is switched back to 'trap' mode. Then a valve is opened, which allows a secondary source of helium to flow at a rate of ~70cc/min to backflush the trap. This flow continues until the next sample is ready to be analyzed.

1.2.7.2.3.7. Data Integration System

The data integration system is performed by a Hewlett Packard Vectra computer in conjunction with the ChromPerfect-5890 Direct chromatographic software program (Justice Innovations, Mountain View, CA). The software program records and stores the

digital voltage signal and the time. The compound peak areas are also quantitatively integrated with their retention time recorded.

Although the software program does a very good job at integrating accurately, it is good procedure to check the integration. A different software program known as HCID (Graham Solutions, Conyers, GA) allows you to check the integration, and manually re-integrate as necessary.

HCID is also used to name the GC peaks and convert peak areas to ppbC. This software allows the use of a file named CALTABLE, which contains approximately 300 compounds retention times, Retention index and compound name. This information has been determined from a number of complex ambient air samples and VOC mixtures. These retention times are matched to the retention times of the sample chromatogram if the retention time is within a selectable tolerance range. To ensure accuracy of this procedure, reference peaks are manually selected and their retention times are compared with the CALTABLE retention time. The CALTABLE retention time is adjusted by the ratio of the observed sample retention time to the CALTABLE value.

1.2.7.3. GC-MS

In order to confirm the accuracy of the peak naming procedure or to identify unknown compound peaks a gas chromatogram is used in conjunction with a mass spectra detection system (GC/MS). The analytical instruments are a Hewlett-Packard Gas Chromatograph Model 6890 combined with a Hewlett Packard Model 5972 Mass Selective Detector. The same column, temperature program, and pre-concentration

system are used for the GC-MS as the GC-FID. A difference between the systems is the use of an electronic pressure control device to keep the helium carrier flow rate constant at 1.4 cm^3/min, throughout the temperature program. For this to occur the pressure changes with column temperature. At 75^oC, the pressure is measured as 67 kPa.

1.2.7.3.1. Theory of Operation

After the compounds have been separated by the column, they flow through a MS interface line, which is heated to a temperature of 275^oC. Next they enter a vacuum controlled electron impact ion source at -70 eV. The compounds then collide with the high energy electrons. This collision results in fragmentation of the compound. Each compound fragments into an ion pattern that is unique to each compound. Next the ions flow to a quadrupole system. The quadrupole system focuses each individual ion, allowing detection by an ion detection system. The data is processed and the fragment ion patterns are compared to a reference library. The NBS75K reference library is used, which contains the fragmented ion spectra patterns for over a 1000 compounds.

1.3. OBJECTIVES

The objectives of this research are:

1. To make measurements of H_2S emissions from both an anaerobic lagoon and barn at a swine CAFO, using the 450C pulsed fluorescence analyzer.
2. Evaluate H_2S emissions with respect to diurnal and seasonal variations, as well as the effects of meteorological and physicochemical parameters.

3. To develop a process based model to predict H_2S emissions from manure surfaces.
4. Evaluate the accuracy of the process based model by comparing the model emissions to the measured lagoon emissions.
5. To make measurements of RSC and NMVOC emissions from the lagoon and barn, using SUMMA and fused-silica lined canisters. The recovery performance of RSCs in the two types of canisters will be evaluated by performing a stability test.
6. Evaluate RSC and NMVOCs emissions with respect to seasonal variations, as well as the effects of meteorological and physicochemical parameters.
7. Determine the potential environmental impact of RSC and NMVOC swine CAFO emissions by comparing concentrations to their odor threshold, calculating North Carolina swine CAFO emissions, identifying the number of hazardous air pollutants, and the potential of NMVOCs to form ozone.

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Table 1.1. Sources and sinks of the global sulfur cycle (Units = Tg S yr^{-1}).

Reference	Schlesinger, (1997)	Warneck, (1988)	Seinfield and Pandis, (1998)[a]
Source			
Anthropogenic Emissions	90	106	73-80
Oceans	16	36	15-25
Biogenic emissions (land)	4	7	0.25-2.78
Volcanoes	10	7	9.3-11.8
Sea Spray	144	150	-
Mineral Dust	8	-	-
Total	**270**	**306**	**98-120**
Sink			
Ocean deposition	**180**	178	-
Land deposition	**90**	128	-
Total	**270**	**306**	

[a] Estimate just includes sources

Table 1.2. A summary of global NMVOC emissions

Type of Source	Emission rate (Tg year^{-1})[a]	Compounds groups[a]	Main Compounds
Anthropogenic			
Petroleum-related sources and chemical industry	36-62	Alkanes, alkenes, and aromatic compounds	[b]Ethylene, toluene, benzene, m-p-xylene, i-pentene, n-pentane, n-butane, i-butane
Natural gas	2-14	Light alkanes	[b]Ethane, propane, n-pentane, i-pentane
Organic solvent use	8-20	Heavy alkanes and aromatic compounds	[b]Toluene, ethanol, and m-p -xylene
Biomass burning	25-80	Light alkanes and alkenes	[c]Ethane, propane, propene, and acetylene
Biogenic			
Vegetation-Isoprene	175-503	-	-
Vegetation-Monterpenes	127-480	-	[d]α- Pinene, β-Pinene
Vegetation- other	510	Heavy alkanes, alkenes, alcohols, aldehydes, ketones and esters	[d]Methanol, Ethene, Propene, ethanol, acetone, hexenal
Ocean	2.5 -6	Light alkanes and alkenes	[a]Ethane, propane, ethene, propene,
	0-26?	C_9-C_{28}	-
Soil	<3	-	[a]Ethene

[a] Warneck (2000)
[b] Nelson et al. (1983)
[c] Radke et al. (1991)
[d] Guenther et al. (2000)

Table 1.3. RSCs odor thresholds and characteristics

Compound	Odor Threshold (ppb)	Odor Characteristic
Hydrogen Sulfide (H_2S)	17.8[a], 4.5[b], 8.1[c]	Rotten eggs
Dimethyl Sulfide (CH_3SCH_3)	2.24[a], 9.8-20[d]	Stench
Dimethyl Sulfide (CH_3SSCH_3)	12.3[a], 0.78-3.6[d]	Putrid, garlic
Methyl Mercaptan (CH_4SH)	1.05[a], , 0.54[b], 1.6[d]	Rotten cabbage
Carbon disulfide (CS_2)	9.55[a]	ND

ND – Not described

[a] Devos et al. (1990)

[b] Odor Threshold, American Industrial Hygiene Association (1989)

[c] Amoore and Hautala (1983)

[d] Haz-Map (2007). Note: The reference for this odor threshold was not provided

Table 1.4. NMVOC odor threshold and characteristics

Compound	**Odor Threshold (**ppb)	**Odor Characteristic**
Butanoic Acid	3.89[1]	Sweaty, Rancid
Pentanoic Acid	4.79[1]	Unpleasant
3-methylbutanoic Acid	2.46, 0.359[2]	Body Odor, acidic
2-Methylbutanoic acid	1.86[1]	Stench
Pelargonic Acid	1.91[1]	ND
Octanoic Acid	3.98[1]	Unpleasant, Rancid
Decanoic Acid	8.7[1]	ND
1-Octanol	5.75[1]	Earth, moldy
Butanal	8.91, 5.23-65.4[2]	ND
3-methylbutanal	2.24[1]	Pungent, Apple like
Heptanal	4.79. 53.5[2]	ND
Octanal	1.35, 1.11-2.59[2]	Aldehydic
Nonanal	2.24[1], 0.77-2.08[2]	ND
Decanal	0.89[1]	ND
Salicyaldehyde	7.41[1]	ND
Trimethylamine	2.40[1]	Fishy, Pungent
Ethylbenzene	2.88[1]	ND
2-3-Butanedione	4.37[1], 1.42-7.39[2]	Chlorine like, butter like
2,3 Pentanedione	5.13[1]	acetone
2-Decanone	7.94[1]	ND
Indole	0.03[2]	Intense fecal, nauseating
Skatole	0.56[2]	Fecal odor, nauseating
4-methylphenol (p-Cresol)	1.86[1], 0.06793-0.264[2]	Phenloic, Barnyard
3-methylphenol (m-Cresol)	0.794[1]	ND
2-methylphenol (o-Cresol)	1.70[1]	ND
o-Methoxyphenol	1.0[1]	ND
Hexanal	13.8, 7.3-12.9[2]	ND

[1] Devos et al. (1990)

[2] Rychlik et al. (1998)

ND = No description of odor characteristic

Table 1.5. H_2S fluxes from previous swine CAFOs lagoon studies .

Reference	Location	Sampling Period	Lagoon Temperature (^oC)	pH	Sulfide Concentration ($mg\ L^{-1}$)	H_2S flux ($\mu g\ m^{-2}\ min^{-1}$)
Zahn et al. (2001)	MO	August	-	8.1	15	438
Zahn et al. (2001)	MO	September	-	8.2	17	492
Zahn et al. (2001)	MO	October	-	8.1	18	1266
Lim et al. (2003)	Midwest[1]	April-July	25	8.1	-	546
Lim et al. (2003)	Midwest[1]	April-July	25	7.9	-	138
Byler et al. (2004)	NE	May-June	-	7.8	-	114
Byler et al. (2004)	NE	May-June	-	7.4	-	192
Byler et al. (2004)	NE	July-August	-	8.1	-	4.2
Byler et al. (2008)	NE	July-August	-	7.7	-	19.2
Blunden and Aneja (2008)	NC	October-November	18	8.1	0.6	0.3
Blunden and Aneja (2008)	NC	February	12	8.1	3.2	~0.0
Blunden and Aneja (2008)	NC	April	15	8.1	1.8	0.5
Blunden and Aneja (2008)	NC	June	30	8.0	9.2	5.3

[1] Location is assumed to be Midwest of U.S, as location is not specified in paper.

Table 1.6. Barn H_2S concentrations and emissions from previous swine CAFO studies.

Reference	Location of study	Ventil-ation type	Manure collection system	Month	ADM Conce-ntrat-ion (ppb)	Total live animal weight (kg)	Emission rate (H_2S g day^{-1} AU)
Heber et al. (1997)	Midwest[1]	NV	Deep pit	Jan-Mar	180	-	0.84
Ni et al. (2002)	IL	MV	Deep pit	Jun-Sep	173	48,783	8.3
Zhu et al. (2000)	Midwest[1]	MV	Deep pit	Sep	414	44,990	2.0[3]
Zhu et al. (2000)	Midwest[1]	NV	Deep pit	Sep	271	43,640	3.32[3]
Jacobson et al. (2003)	MN	NV	Deep bedded	Dec	10.1[2]	-	0.11[4]
Jacobson et al. (2003)	MN	NV	Deep bedded	Jun-Jul	8.7	-	0.16[4]
Heber et al. (2004)	Midwest[1]	MV	Shallow pit/Flush daily	Aug-Nov	141[2]	79,650	1.34
Heber et al. (2004)	Midwest[1]	MV	Shallow pit/Flush daily	Dec-Mar	73.5	74,324	0.35
Heber et al. (2004)	Midwest[1]	MV	Shallow pit/Flush daily	May-Aug	171	94,329	0.80
Kim et al. (2008)	S. Korea	NV	Deep pit	May-Jun & Sep-Oct	296.3[2]	-	6.7[3]
Kim et al. (2008)	S. Korea	MV	Deep pit	May-Jun & Sep-Oct	612.8	-	8.5
Kim et al. (2008)	S. Korea	NV	Scraper removal	May-Jun & Sep-Oct	115.2	-	5.8
Kim et al. (2008)	S. Korea	MV	Scraper removal	May-Jun & Sep-Oct	270.3	-	6.3
Kim et al. (2008)	S. Korea	NV	Deep bedded	May-Jun & Sep-Oct	137.8	-	3.0
Blunden et al. (2008)	NC	MV	Shallow pit/Flush weekly	Feb	632	48,963	4.2
Blunden et al. (2008)	NC	MV	Shallow pit/Flush weekly	Apr	441	73,895	3.3
Blunden et al. (2008)	NC	MV	Shallow pit/Flush weekly	Jun	47	33,952	1.2
Blunden et al. (2008)	NC	MV	Shallow pit/Flush weekly	Oct	304	38,390	1.7

ADM = average daily mean

[1] Location is assumed to be Midwest of U.S., as location is not specified in paper

[2] Concentrations presented from this study are average concentrations, instead of average daily mean concentrations

[3] Emissions calculated for this study are based on data presented in the paper

[4] Emission numbers for this study are based on comment in Jacobson et al. (2004)

Table 1.7. Concentration of RSCs from previous swine CAFOs studies.

Reference	Location	Manure collection system/description of sample location	Vent system	Facility type	Month	Concentration (ppb)			
						CH_3SH	DMS	CS_2	DMDS
Clanton and Sch (2000) [a]	MN	Deep pit sim[c]/room air	M	Grow/Finish	Apr	27	2.2	45	3.9
Clanton and Sch (2000)	MN	Deep pit sim[c]/room air	M	Grow/Finish	Apr	10	5.1	25	1.2
Clanton and Sch (2000)	MN	Deep pit/pit fan	M	Gestation	Apr	ND	2.2	17	-
Clanton and Sch (2000)	MN	Pull plug/wall fan	M	Nursery	May	ND	ND	14	ND
Clanton and Sch (2000)	MN	Pull plug/room air	M	Nursery	May	7	ND	26	ND
Clanton and Sch (2000)	MN	Pull plug/pit fan	M	Nursery	May	ND	ND	8	ND
Trabue et al. (2008a)	IA	Pull plug/room air	M	Finish	NS	ND	ND	27.8	ND
Trabue et al. (2008a)	IA	Pull plug/room air	M	Farrow	NS	ND	ND	13.1	ND
Trabue et al. (2008a)	IA	Deep pit/pit fan	N	NS	NS	6.84	5.3	2.4	<LOQ
Kim et al. (2007)	S. Korea	Deep pit/room air near fan outlet	M	Gestation	Mar-May & Sep-Nov	4.8	2.1	-	0.9
Kim et al. (2007)	S. Korea	Deep pit/room air near fan outlet	M	Farrow	Mar-May & Sep-Nov	4.0	2.0	-	1.2
Kim et al. (2007)	S. Korea	Deep pit/room air near fan outlet	M	Nursery	Mar-May & Sep-Nov	5.6	2.3	-	1.4
Kim et al. (2007)	S. Korea	Deep pit/room air near fan outlet	M	Grow	Mar-May & Sep-Nov	10.8	6.0	-	3.4
Kim et al. (2007)	S. Korea	Deep pit/room air near fan outlet	M	Finish	Mar-May & Sep-Nov	16.0	8.4	-	4.7
Blunden et al. (2005)	NC	Shallow pit/ [b]	M	Finish	Oct	-	0.2	-	0.1
Blunden et al. (2005)	NC	Shallow pit/ [b]	M	Finish	Feb	-	0.1	-	0.2
Blunden et al. (2005)	NC	Shallow pit/ [b]	N	Finish	Sep	-	1.6	-	0.2
Blunden et al. (2005)	NC	Shallow pit/ [b]	N	Finish	Jan	-	ND	-	ND

ND = No detection, NS = Not specified, [a] full reference is Clanton and Schmidt, (2000), [b] sample taken outside of barn near fan, [c] full description of manure collection system is Deep pit simulation

Table 1.8. HAPs identified by Schiffman et al., (2001), and also by other swine CAFO studies.

HAPs identified by Schiffman et al. (2001)	Studies that have identified HAPS at swine CAFOs
Hexanal	
4-methylphenol (p-cresol)	Trabue et al. (2008b), Zahn et al. (1997), Blunden et al. (2005)
3-methylphenol (m-cresol)	Zahn et al. (1997)
2-methylphenol (o-cresol)	
Acetaldehyde	Blunden et al. (2005)
Acetamide	
Acetonitrile	
Benzene	
Dibutylphthalate	
Ethyl benzene	
Formaldehyde	
Hexane	Blunden et al. (2005)
Methanol	
Methyl ethyl ketone	
Methyl isobutyl ketone	
Dichloromethane	
Napthalene	
Phenol	Trabue et al. (2008b), Zahn et al. (1997)
Toluene	
Trichloroethylene	
Triethylamine	
Vinyl acetate	

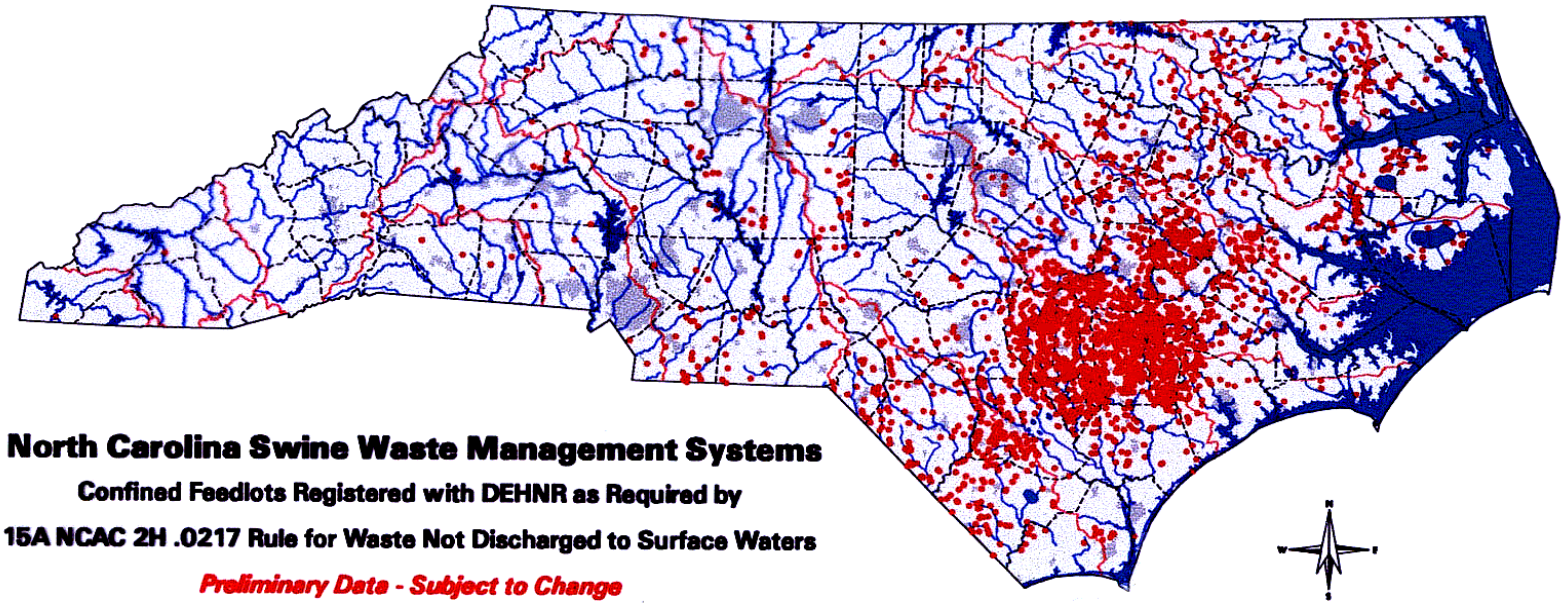

Figure 1.1. Map indicating the location of swine farms in North Carolina.

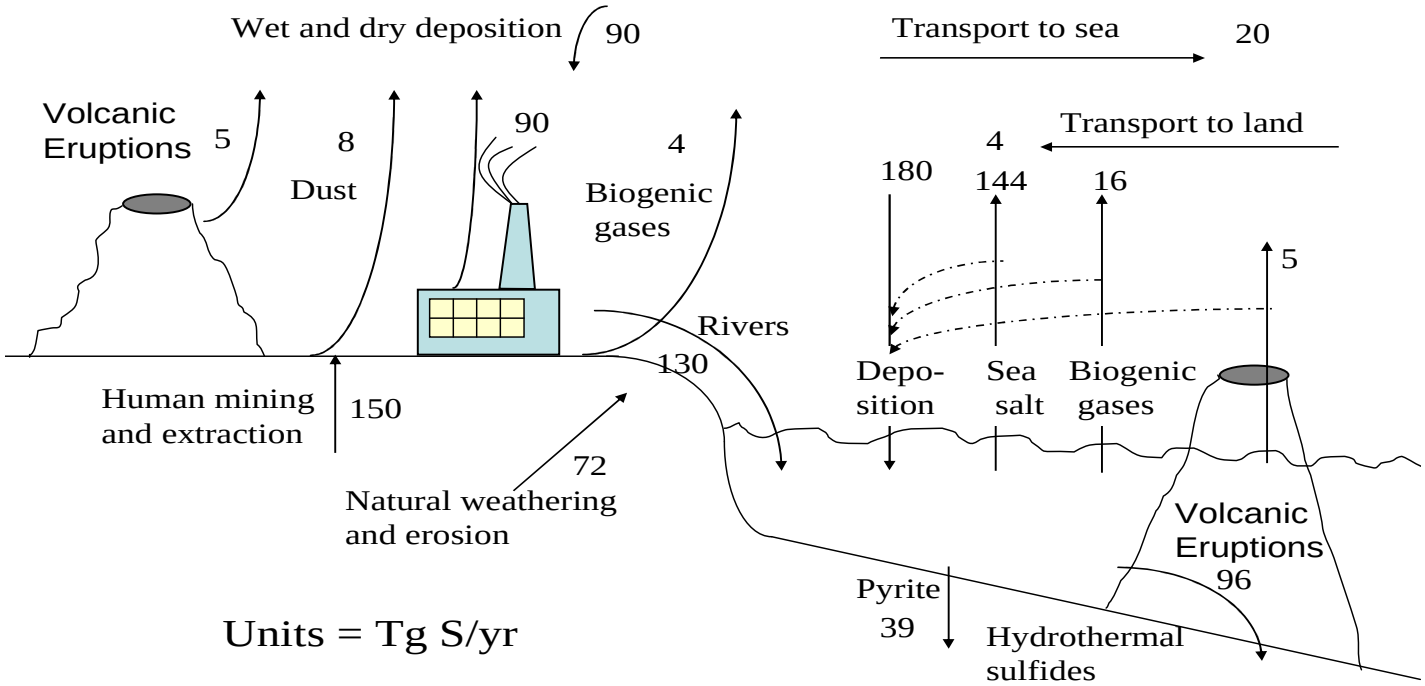

Figure 1.2. The global sulfur cycle, adapted from Schlesinger (1997), T = 10^{12}.

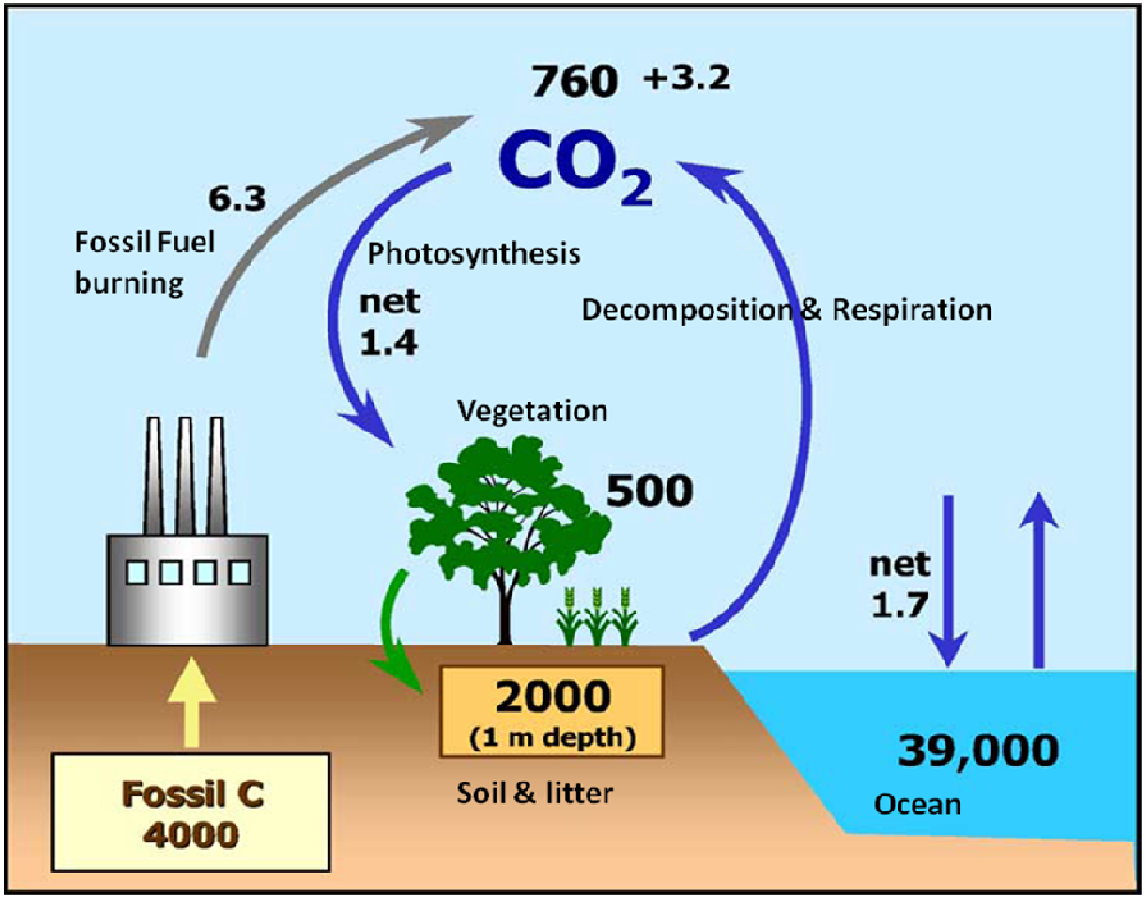

Figure 1.3. The modern global carbon cycle. Units are in Pg C or Pg C yr^{-1}(from: Janzen, 2004).

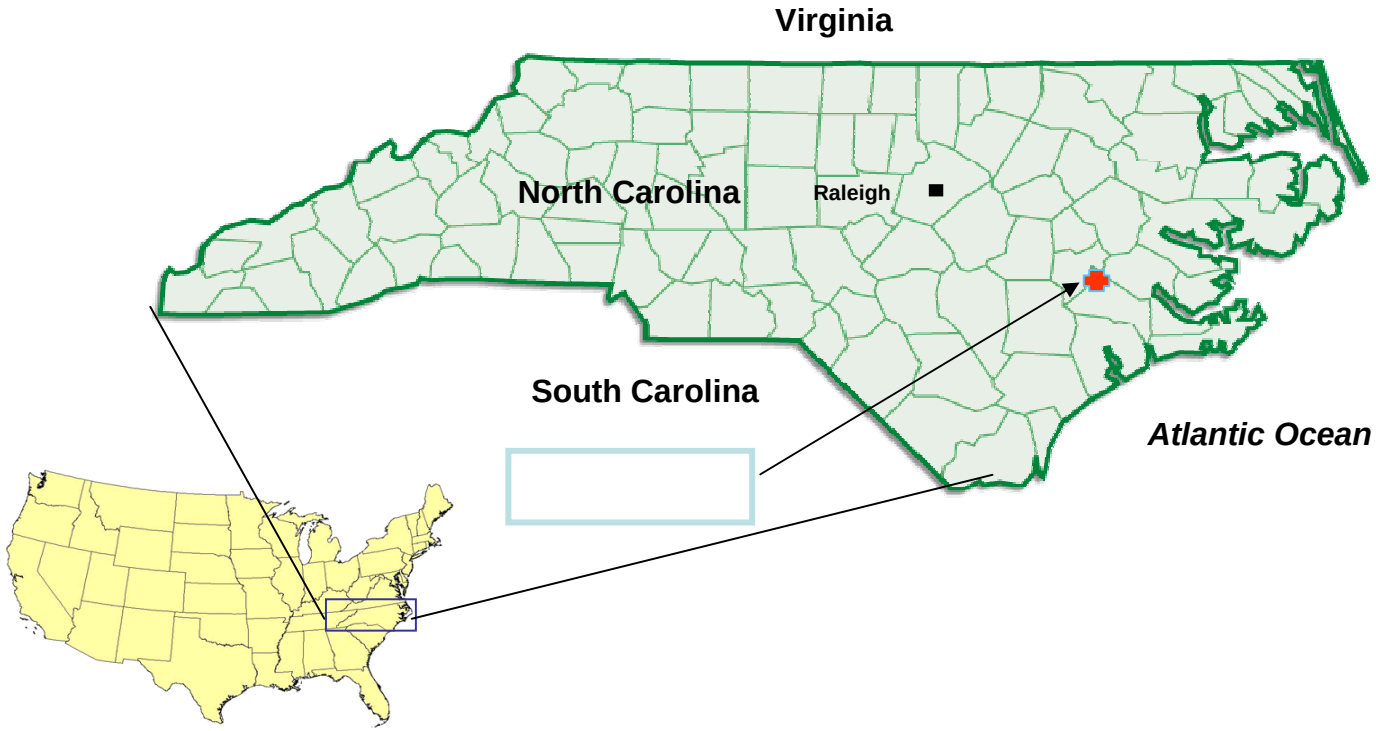

Figure 1.4. Location of swine CAFO.

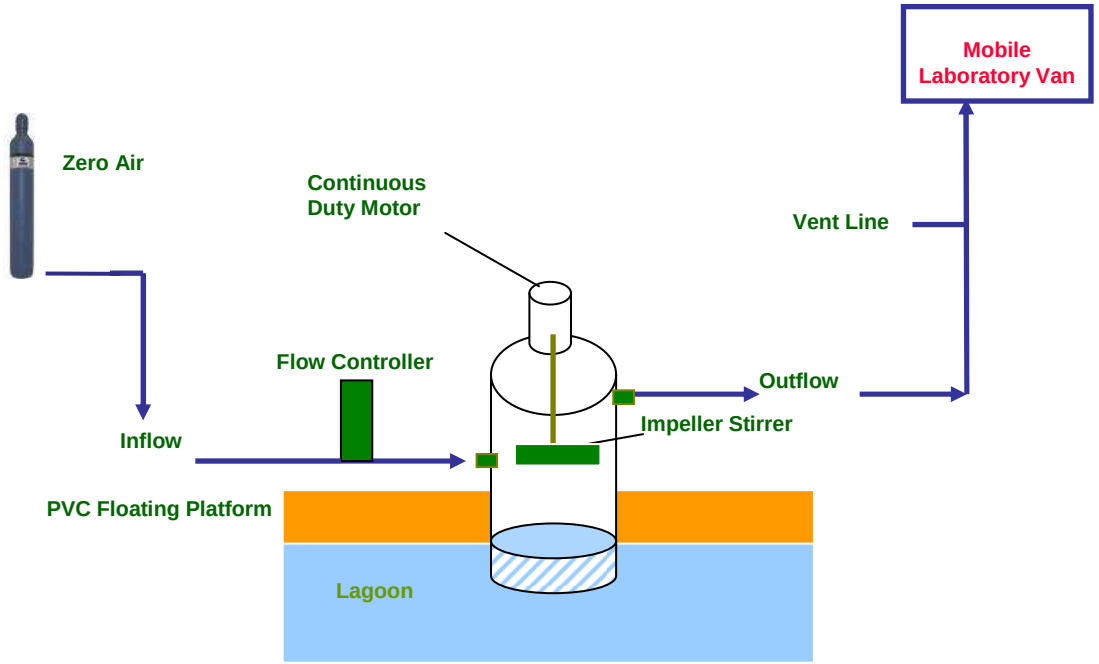

Figure 1.5. Schematic of the dynamic flow-through chamber system.

Figure 1.6. Photograph of the dynamic flow-through chamber system and supporting platform.

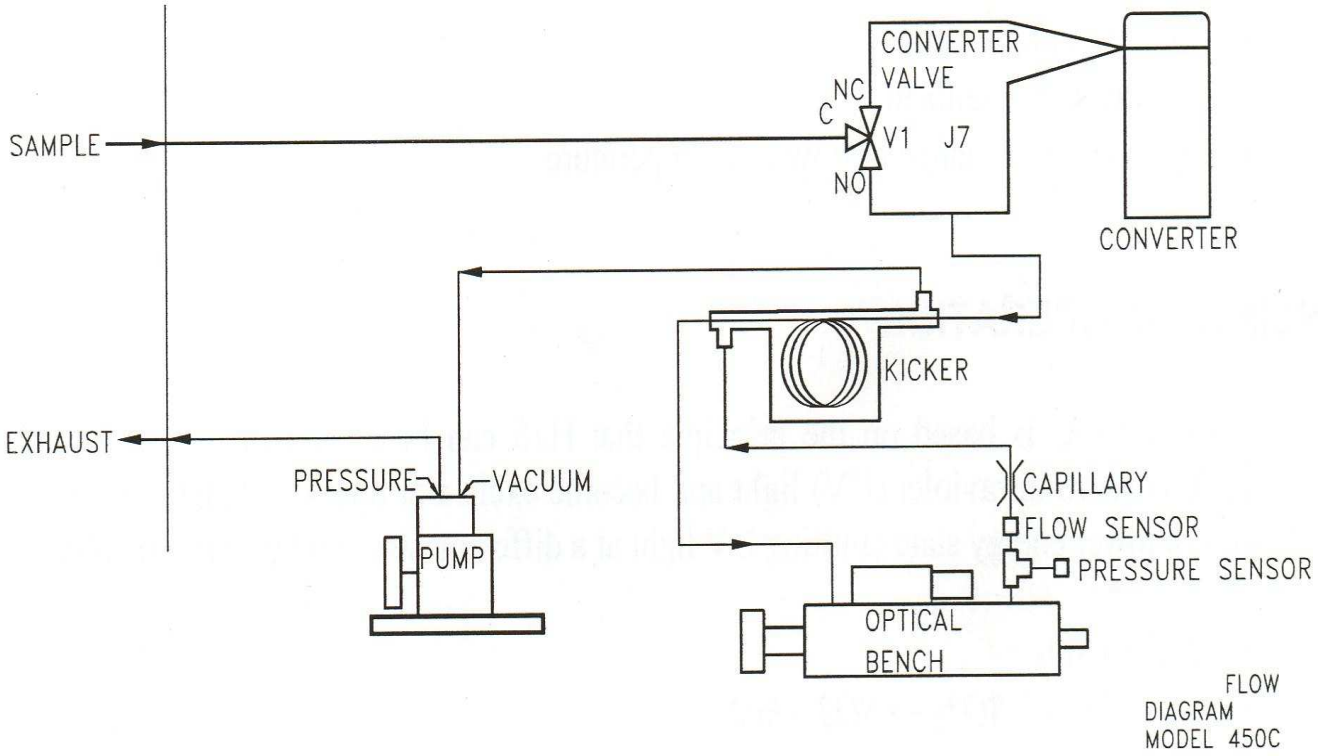

Figure 1.7. Schematic of the TEI 450C H_2S/SO_2 analyzer flow system (from: TEI, 2002).

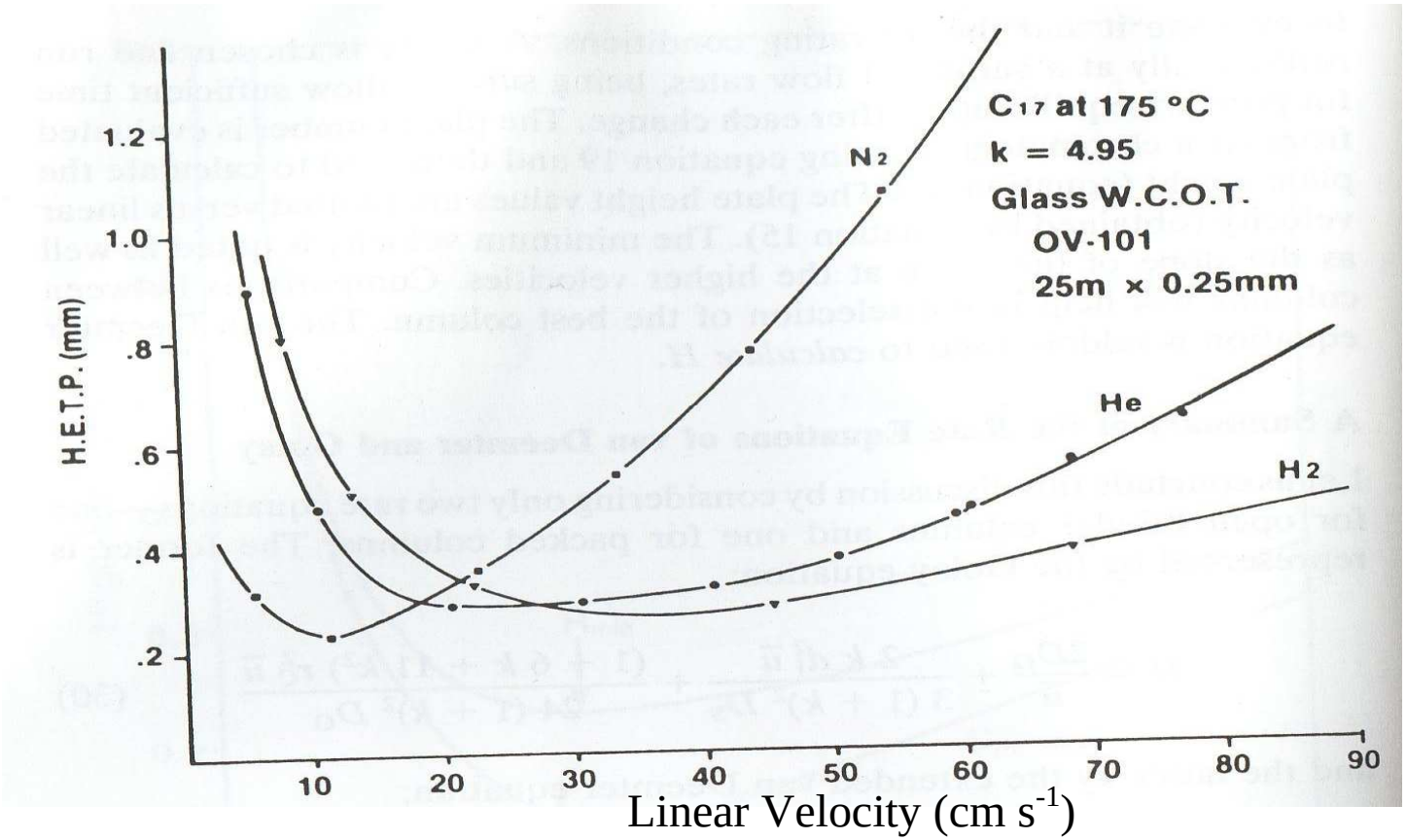

Figure 1.8. Effect of different carrier gas and velocities on a typical van Deemter curve (from: McNair and Miller, 1998). H.E.T.P = Height equivalent to one plate.

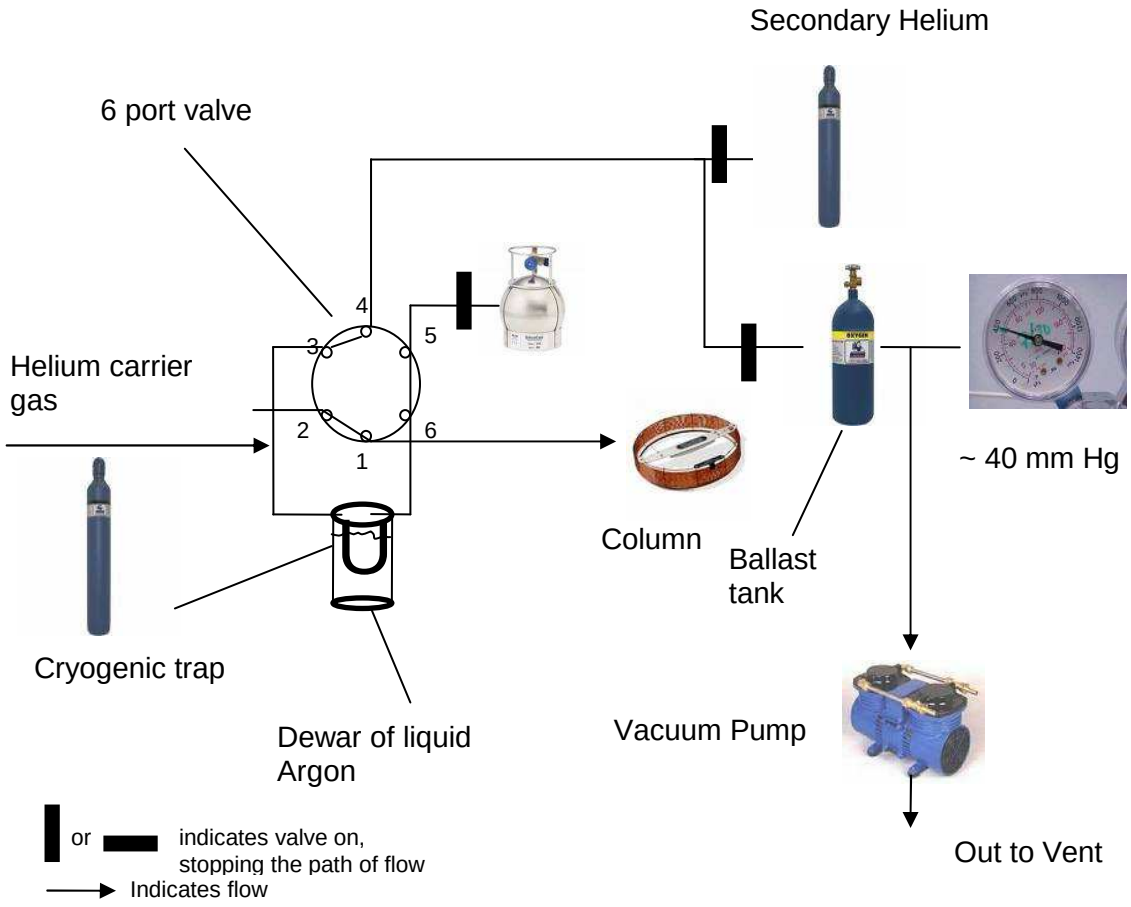

Figure 1.9a. Stage 1 of the GC-FID analysis.

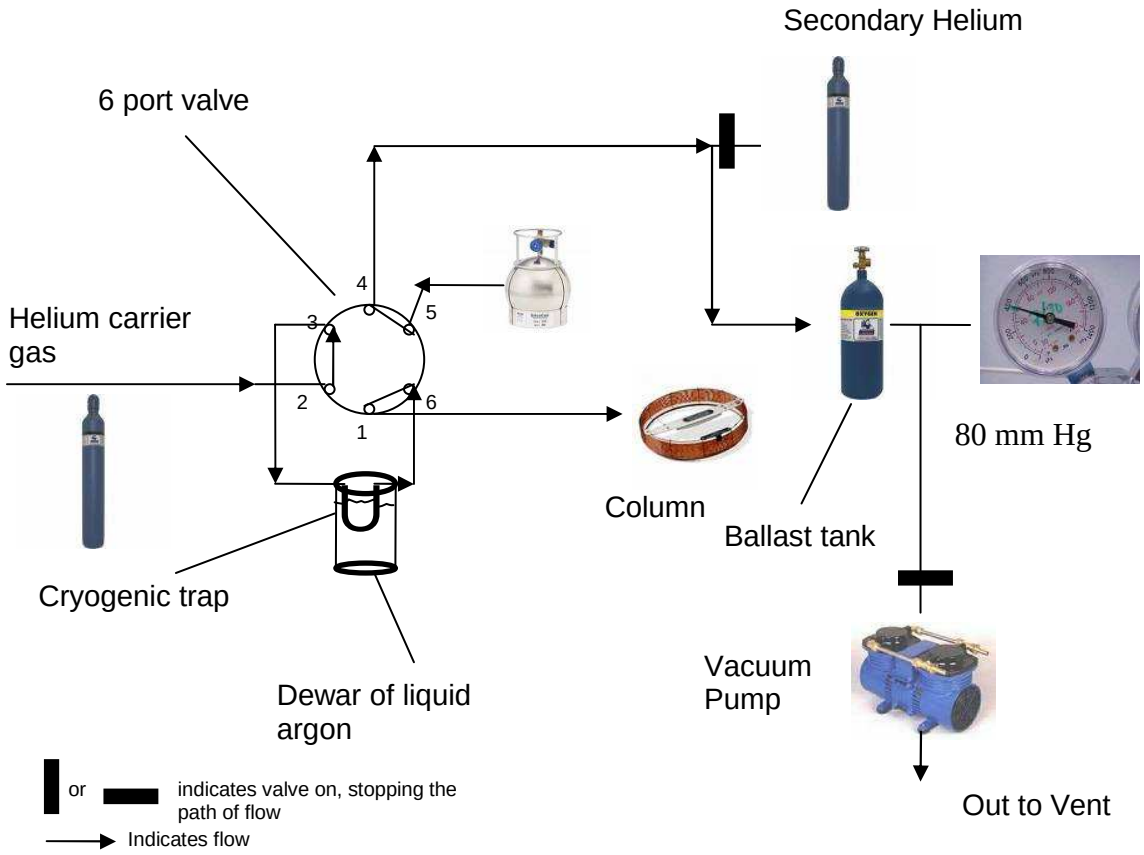

Figure 1.9b. Stage 2 of the GC-FID analysis.

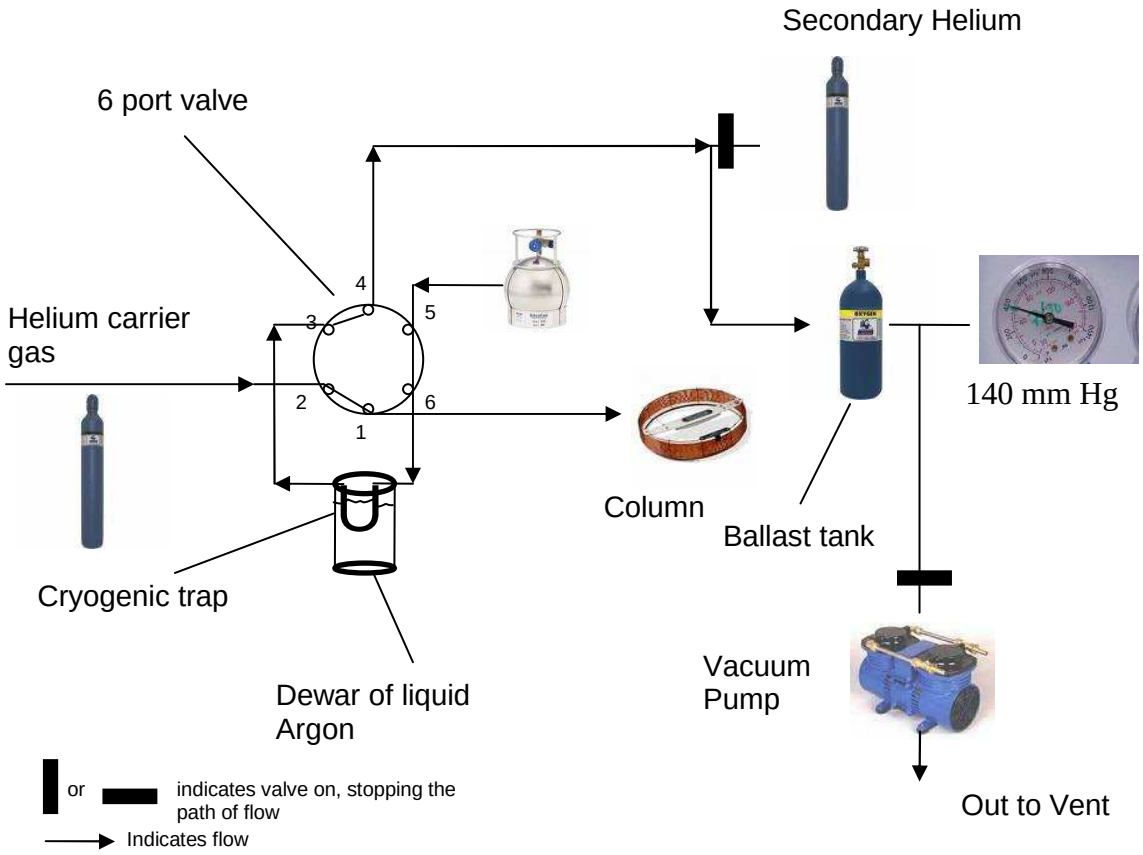

Figure 1.9c. Stage 3 of the GC-FID analysis.

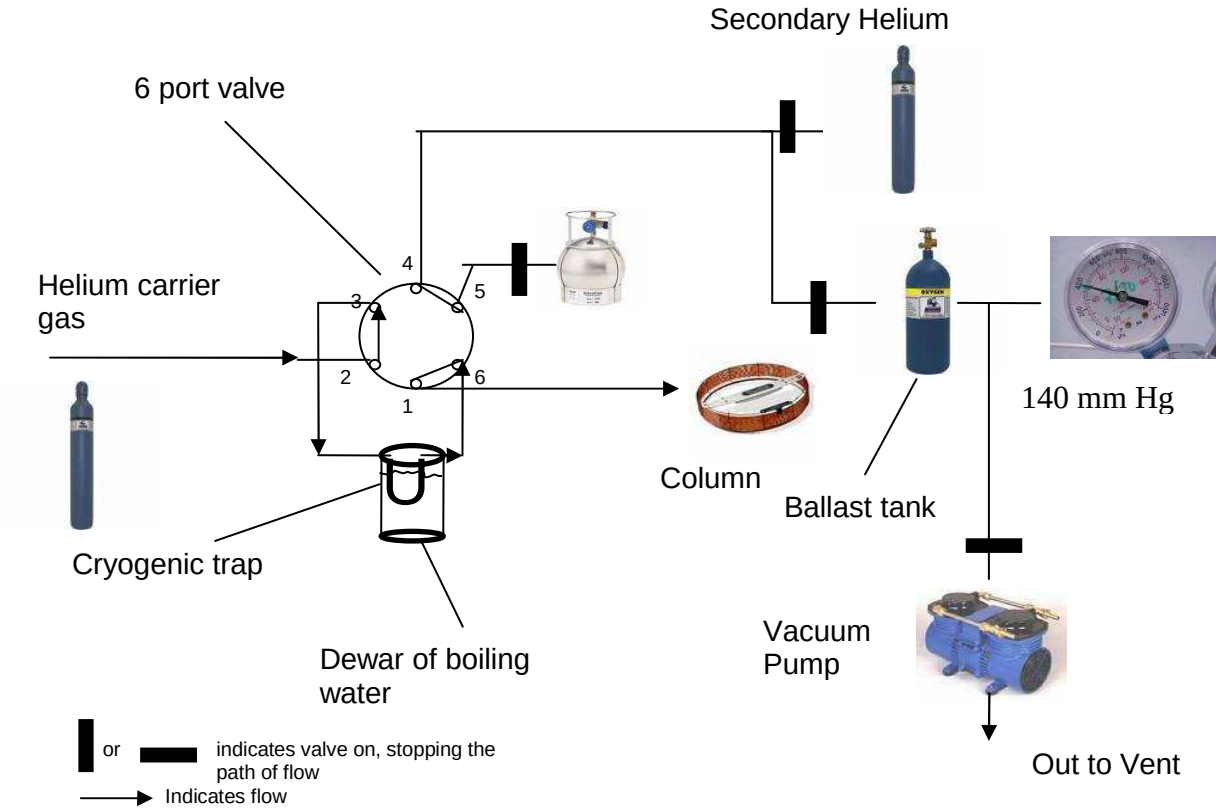

Figure 1.9d. Stage 4 of the GC-FID analysis.

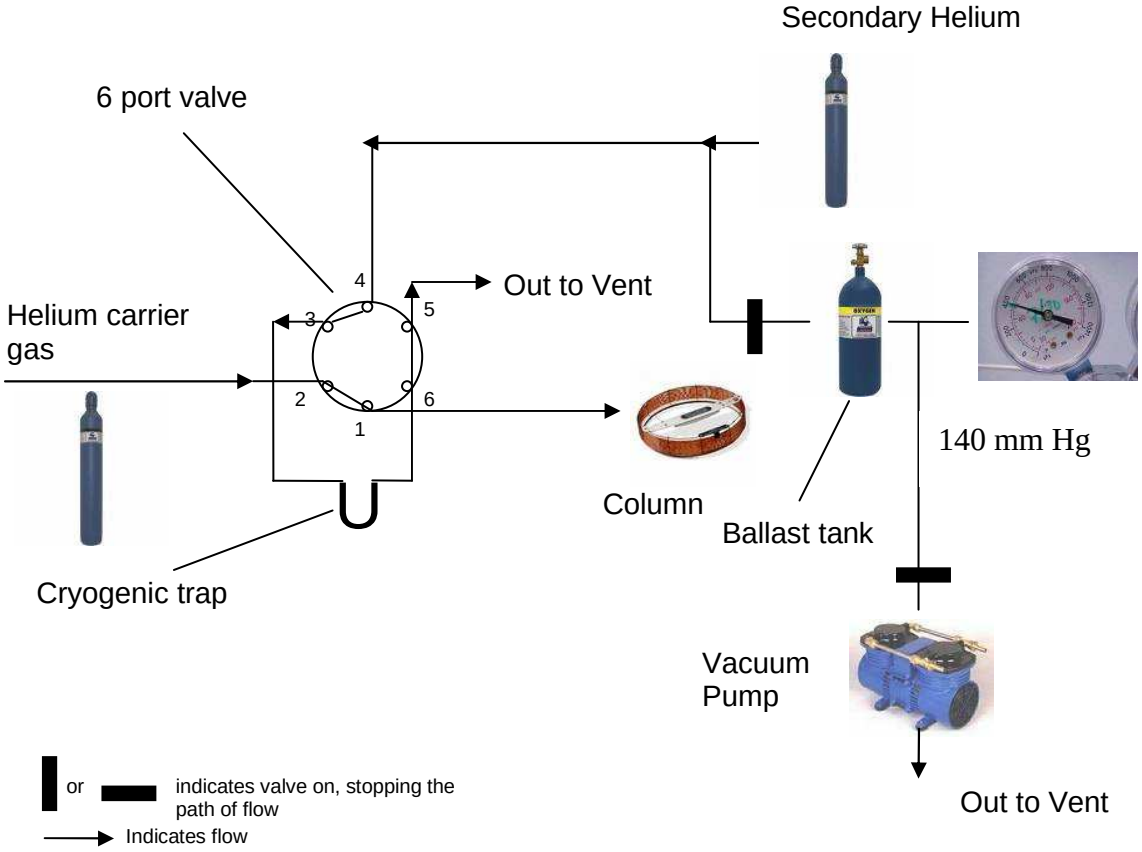

Figure 1.9e. Stage 5 of the GC-FID analysis.

CHAPTER II.
Measurement and Modeling of Hydrogen Sulfide Emissions from a Swine Concentrated Animal Feeding Operation

ABSTRACT

Hydrogen sulfide (H_2S) emissions from concentrated animal feeding operations (CAFOs) are an important concern due to their contribution to odor and their potential to form fine particulate matter (PM_{fine}). H_2S emission measurements were made from an anaerobic lagoon and barn at a swine CAFO in North Carolina. H_2S measurements were made continuously for a ~1 week period from both the anaerobic lagoon and barn during each of the four seasonal periods during the period June 2007 through April 2008. During the sampling periods, continuous measurements of physiochemical and meteorological factors were made. H_2S lagoon fluxes were highest in the summer with a flux of 3.82 ± 3.24 μg m^{-2} min^{-1}, and lowest in the winter with a flux of 0.08 ± 0.09 μg m^{-2} min^{-1}. Lagoon pH was found to have the largest influence on H_2S lagoon fluxes, followed by lagoon temperature and wind speed. Seasonal H_2S barn concentrations were highest in the spring with a concentration of 631 ± 240 ppb. The lowest seasonal H_2S barn concentration was 72 ± 43 ppb, which occurred in the summer sampling period. Seasonal barn emissions were found to range from 0.81 ± 0.48 g day^{-1} AU^{-1} in the winter to 7.31 ± 2.48 g day^{-1} AU^{-1} in the spring. H_2S manure emissions were modeled using a process based air-manure interface (A-MI) mass transfer model. Different approaches were used to calculate the three main components of the A-MI mass transfer model: the dissociation constant, the Henry's law constant and the overall mass transfer coefficient. The

dissociation constant was calculated based on thermodynamic principles and was corrected for the ionic strength (i.e. electrical conductivity) of the manure. Similarly, the Henry's law constant was also calculated based on thermodynamic principles. The overall mass transfer coefficient was developed based upon a previously published study's experimental measurement of the overall H_2S mass transport coefficient. The A-MI mass transfer model predicted fluxes were compared with measured H_2S flux using meteorological and physiochemical measurements made from the anaerobic lagoon. The A-MI mass transfer model performed fairly well in comparison to 15 minute average lagoon fluxes ($r^2 = 0.57$, $p<0.0001$) and average seasonal lagoon fluxes. It is hypothesized that with appropriate information on the overall mass transport coefficient, that the model could be applied to predict CAFO trace gas emissions from different manure surfaces, therefore providing a method for quantifying emissions in different production, management and environmental conditions.

2.1. INTRODUCTION

The intensification of animal agriculture to meet the food demands of an increasing world population, have resulted in a number of environmental concerns. These concerns include emissions of nitrogen, sulfur and volatile organic compounds and particulate matter from concentrated animal feeding operations (CAFOs) into the atmosphere (Aneja et al., 2008).

Within the last 20 years, there have been changes in livestock methods in North Carolina, owing to economic pressures. This has resulted in the growth of swine CAFOs. Between 1987-1997, the swine population rose rapidly from ~2.5 million to ~10 million. This expansion was curtailed by a moratorium issued by the North Carolina State Legislator, which did not allow the building of new swine farms or the expansion of existing swine farms, unless a more stringent environmental criteria could be met (House Bill 515; S.L. 1997-458). Additionally, during a similar time period, the number of swine operations has decreased, from 18,000 in 1985 to currently ~ 2800 (United States Department of Agriculture (USDA), 2009). The development of a large number of swine CAFOs have resulted in North Carolina being an area of potential environmental concern.

The main sulfur compound emitted from CAFOs is hydrogen sulfide (H_2S), which is a colorless, potentially harmful gas (US EPA, 2003), with an odor characteristic described as ‘rotten eggs’ (Schiffman et al., 2001). H_2S emissions occur from animal waste as a result of anaerobic microbial decomposition of sulfate. CAFO emissions of odorous compounds such as H_2S are important as they can result in health symptoms and

furthermore health effects (Schiffman and Williams, 2005) and affect the quality of life for people in the surrounding area (Thu et al., 1997; Wing and Wolf, 2000). A further environmental issue associated with H_2S emissions is the formation of particulate matter. H_2S has an atmospheric lifetime of 2-3 days (Seinfield and Pandis, 2006; Warneck, 2000), and can react to form sulfur dioxide (SO_2), which in turn can react to form ammonium sulfate or ammonium bi-sulfate. Particulate matter in the form of PM_{fine} (particulate matter with an aerodynamic diameter equal or less than 2.5 μm) has been associated with adverse health effects including premature mortality (Pope et al., 2002). Particulate matter can also additionally impair visibility (Malm et al., 2004; Seinfeld and Pandis, 1998) and scatter incoming solar radiation resulting in regional cooling (Lovelock et al., 1972).

In the U.S. there are two main areas of swine production, the Midwest and North Carolina. There have been many studies in the Midwest of H_2S emissions from barns with different swine management systems (Heber et al., 1997; Ni et al., 2002; Zhu et al., 2000; Jacobson et al., 2003; Jacobson et al., 2004; Heber et al., 2004) and from lagoons (Zahn et al., 2001, Lim et al., 2003, Byler et al., 2004). However, due to differences in production, management, and environmental conditions, there must also be comprehensive measurements of H_2S swine CAFO emissions in North Carolina. Presently, H_2S swine CAFO emissions in North Carolina has not been studied extensively. Blunden et al. (2008) and Blunden and Aneja (2008) are the only known studies that have measured lagoon and barn H_2S emissions from a swine CAFO in North Carolina. In these studies, measurements from the lagoon and barn were made over four

different sampling seasons. Therefore, further measurements are needed to assess the magnitude of H_2S emissions and the effects of production, management and environmental conditions. This study continues and builds upon the work of Blunden and Aneja (2008) and Blunden et al. (2008) by measuring an additional four seasons of lagoon and barn H_2S emissions at the same commercial swine farm in eastern North Carolina. This paper presents the lagoon and barn H_2S emissions from the four sampling seasons and evaluates them with respect to diurnal and seasonal variations, as well as the effects of meteorological and physicochemical parameters.

As discussed, swine CAFO emissions vary due to difference in production, management and environmental conditions. Therefore there is a need for process based models, which provide a method for quantifying manure emissions in these different conditions. There have been process-based models developed for the manure emissions of another important agricultural trace gas, ammonia (Ni, 1999 and references therein; Aneja et al., 2001; DeVisscher et al., 2002; Liang et al., 2002; Bajwa et al., 2006), however there is only one known study that has modeled H_2S manure emissions, which was conducted by Blunden et al. (2008). In this study, process based models were developed that showed good prediction of H_2S trends, but overestimated the magnitude of emissions.

In this paper, different approaches are used to develop a process based air-manure surface interface mass transfer model. These approaches use thermodynamic principles and related published information to determine the three main components of the air-manure interface (A-MI) mass transfer model: the overall mass transport

coefficient, the dissociation constant, and the Henry's law constant. The accuracy of the A-MI mass transfer model in predicting H_2S manure emissions is evaluated by comparing the model predicted emissions to the measured lagoon emissions described in this paper.

2.2. METHOD AND MATERIALS

2.2.1. Sampling Site

The sampling site is a commercial swine CAFO located in eastern North Carolina, in Jones County. At the swine CAFO, there are eight finishing barns with between 900-1000 pigs in each barn. Generally, the pigs weigh between 20-24 kg on arrival, and stay at the barn for 16-20 weeks. The barns are mechanically ventilated.

The swine CAFO uses a conventional waste management method, known as 'Lagoon and Spray Technology'. In this method, the swine waste falls through slatted floors into a shallow manure collection pit. The swine waste is then flushed weekly from the shallow pit through pipes into an anaerobic treatment lagoon. Periodically, the anaerobic treatment lagoon waste is sprayed over crop fields for nutrient enrichment. The anaerobic treatment lagoon liquid is also used to flush the barn manure pits. This waste management method is used by the majority of swine CAFOs in North Carolina.

2.2.2. Sampling Scheme

Measurements of H_2S emissions were made during all four seasonal periods during the period June 2007 through April 2008. Emissions from both the lagoon and barn were each measured for a ~ 1week period during the sampling seasons. Sampling

was conducted during the summer season from June 8th-June 28th, 2007; the fall season from the October 20th -November 12th, 2007; the winter season from February 8th-February 29th, 2008; and the spring season from 11th April-April 28th, 2008.

2.2.3. H_2S Instrumentation

A thermo environmental instrument (TEI) model 450C pulsed fluorescence H_2S/SO_2 analyzer (Thermo Environmental Corporation, Mountain View, CA) was used to continuously measure H_2S concentrations. The H_2S/SO_2 analyzer has a range of 0-1000 ppb. Before each sampling period, a multi-point calibration was conducted on the analyzer. This was performed using a TEI model 146 dilution-titration system (Thermo Environmental Corporation, Mountain View, CA). Additionally, zero and span checks were conducted regularly during the sampling periods. These were also performed after each sampling period. It should be noted that SO_2 concentrations were not analyzed at the swine CAFO, as concentrations were negligible.

2.2.4. Flux Measurements

2.2.4.1. Lagoon Measurements

Anaerobic lagoon flux was determined using a dynamic flow-through chamber system (Blunden and Aneja, 2008; Aneja et al., 2000). A schematic of the chamber system is presented in Figure 2.1. The chamber is a cylindrical shape, with an internal height and diameter of 46 cm and 26 cm, respectively. This results in a total volume of

the chamber of ~ 25.4 liters (L). A closed system is formed, as ~7cm of the bottom of the chamber protrudes into the lagoon forming a seal.

The inside of the chamber is lined with ~0.05mm thick fluorinated ethylene propylene (FEP) Teflon. The chamber sits inside a circular hole in a 0.61m x 0.61m floating platform, which is composed of ultra-high molecular weight (UHMW) polyethylene, with a thickness of 1.27 cm. Attached to either side of the platform are two PVC pipes (diameter 15.24 cm, length 168 cm), which provide additional buoyancy.

Into the chamber through Teflon tubing (0.64 cm outer diameter, 0.4 cm inner diameter) flows compressed zero-grade air (Machine and Welding Supply Company, Raleigh, NC) at a flow rate of ~ 4 L min^{-1}. This flow rate is controlled/set by a Model 810–S Mass Trak Flow Controller (Sierra Instruments, Monterey, CA). A variable-speed motor rotates a Teflon impeller inside the chamber at speeds of 40-60 rpm. This ensures that the air is well mixed similarly to ambient air. The out flowing air flows through more Teflon tubing into the H_2S/SO_2 analyzer. The out flowing part of the system has a vent. Any air that is not required by the analyzer or canister exits this vent. Additionally, the vent ensures that the closed system does not become over pressurized. The vent was bubble tested to check for leaks and under pressurization. The fittings used in the system were all made of stainless steel, in order to minimize chemical reactions.

2.2.4.2. Lagoon Flux Calculation

In order to calculate the H_2S flux, the following mass balance equation is used.

$$\frac{dC}{dt} = \left(\frac{qC_o}{V} + \frac{JA}{V}\right) - \left(\frac{L_T A_w}{V} + \frac{q}{V}\right)[C] \qquad (1)$$

where q is the flow rate of carrier gas through chamber (m^3 min^{-1}), C_o is the concentration of H_2S in the carrier gas (μg m^{-3}), J is the H_2S flux (μg m^{-2} min^{-1}), A is the cross sectional area of the top and bottom of the chamber (m^2), V is the volume of chamber above the lagoon surface (m^3), L_T is the loss term (m min^{-1}), which total loss of H_2S in the chamber due to reaction with the inner and upper walls of the chamber, A_w is the surface area of inner and upper walls of the internal chamber (m^2), C is the concentration of H_2S within the chamber (μg m^{-3}).

As mentioned, zero-grade air is used for the carrier gas, therefore $C_o = 0$. Additionally, when the system reaches steady state, the instantaneous change of concentration with time approaches zero, therefore dC/dt = 0. Therefore equation (1) is simplified to the following:

$$J = [C\ ]\left[\frac{L_T A_w}{V} + \frac{q}{V}\right]h \qquad (2)$$

where h is the height of the chamber. The loss term (L_T) has been found to be a factor, when calculating NH_3 fluxes (Blunden and Aneja, 2008). However, the loss term determined experimentally in this study and by Blunden and Aneja (2008) was found to be negligible. This is hypothesized to be the result of H_2S having a lower solubility (Blunden and Aneja, 2008). Therefore equation (2) simplifies to the following:

$$J = [C\ ]\left[\frac{q}{V}\right]h \qquad (3)$$

2.2.5. Barn Measurements

Barn measurements were made at one of the eight swine barns at the sampling site. At the west end of the barn facing the lagoon there are five ventilation fans (AAA.Associates Inc. Maxi-Brute™ fans, Niles, MI). All five fans had plastic shutters. Three are belt driven with a diameter of 122 cm. Two of the fans are direct driven, and have a diameter of 91 cm. The fans turn on in a set sequence, as barn temperature increases. The barn flow rate was calculated using the following equation:

$$Calculated\ fan\ flow\ rate = Manufactures\ fan\ flow\ rate \times \left(\frac{Measured\ RPM}{Specified\ RPM}\right) \quad (4)$$

The measured revolutions per minute (RPM) were determined using a rotation-voltage relationship system (Blunden et al., 2008). Measured revolutions per minute (rpm) were calculated by attaching Mabuchi VDC motors (Santa Clara, CA) to the fans. For the direct driven fan's, the motor was mounted to a stainless plate, which lies over the fan's original plate. For the belt driven fan's, a cylinder sleeve was placed over the fan shaft. From the motors, single analog output wires were used to connect each motor to a data logger (Campbell Scientific CR10X, Logan, UT). Therefore if a fan was rotating, a voltage was recorded. To determine the relationship between voltage and rpm, the motors were calibrated before the beginning of the field campaign using a Dayton SCR controlled DC Motor (Model # 2M168C). The motors were attached to the shaft of the controlled DC motor. From this, simultaneous rpm and voltage were measured using a Shimpo DT-207B Direct Contact Digital Tachometer, a Shimpo DT-725 stroboscopic Digital Tachometer, (Itasca, IL) and a Micronta Digital Multimeter (Model # 22-185).

From this procedure a calibration curve was determined. For every sampling season, the stroboscopic tachometer was used to check and evaluate each fan's performance. From this, the calibration curve was adjusted accordingly for each season.

The manufactures specifications are 850 rpm for the direct drive motors and 1725 rpm for the belt driven motors. However it has been estimated that the pulley ratio is approximately 2:9:1, resulting in the fans rotating at approximately 595 rpm.

Measurements of the static pressure difference were made between the inside and outside of the barn using a hand held pressure sensor. Pressure readings were taken daily during all the sampling seasons. When taking readings, it was noted how many fans were on. These measurements were used to determine the average static pressure difference, when a certain number of fans were on. The manufacturers fan flow rate was adjusted accordingly for the average static pressure difference.

2.2.5.1. Barn Emission Rate Calculation

Barn concentration measurements were made by placing a sample line made of Teflon tubing (0.64 cm outer diameter, 0.4 cm inner diameter) directly in front of the first fan to turn on. The concentration distribution across the fan was assumed to be uniform. Concentrations were assumed to be equal for all barn fans. Background barn samples were collected upwind of the barns using fused-silca lined canisters. Concentrations in background samples were negligible in comparison to the corresponding H_2S concentration from the barn fan, therefore they are not considered in emission calculations. The barn emission rates are therefore defined by the following equation:

$$J = C * \sum f \qquad (5)$$

where J is the H_2S flux, C is the H_2S concentration at the fan, Σf is the sum of the flow rates of each individual fan.

2.2.6. Environmental Parameter Measurements

During lagoon sampling, lagoon temperature and lagoon pH were measured continuously. Lagoon temperature was measured by a CS107 temperature probe (Campbell Scientific Inc., Logan, UT). A model CSIM11 pH probe (Campbell Scientific Inc., Logan, UT) was used to measure lagoon pH. The pH probe is placed in buffer solution and calibrated before and after each sampling period of ~1 week. Both probes are submerged ~7cm below the lagoon surface. For barn sampling, a CS107 temperature probe was used to measure temperature at the fan outlet.

During both lagoon and barn sampling, meteorological measurements of relative humidity (RH), air temperature, and solar radiation were made at a height of 2 m. In addition, measurements of wind speed and wind direction were made at a height of 10 m.

Near-surface (< 10 cm) anaerobic treatment lagoon samples were taken daily to be analyzed for sulfide content. The lagoon samples were preserved for sulfide analysis by adding 1ml of 2N zinc acetate and ~6N NaOH until the pH>9. The samples were stored below 4^oC until analysis. Samples were analyzed within 5 days of collection at the North Carolina Division of Water Quality. Sulfide content was measured color metric analysis. This was performed using Standard Method 4500-S2-D (Greenberg et al., 1999).

A Model CR23X Data logger model and a CR10X Data logger, which has a Model AM 16/32 Channel Relay Multiplexer (Campbell Scientific Inc., Logan, UT) were used to record and collect all data. The data was downloaded to a laptop daily. The datalogger and the H_2S/SO_2 analyzer were housed inside a mobile laboratory (NC State University Air Quality Ford Aerostar Mini-Van). To ensure that the instruments worked efficiently, the temperature inside the mobile laboratory was maintained to room temperature at ~ 21^oC.

2.2.7. Modeling of H_2S Manure Emissions

H_2S manure emissions were modeled by developing a process based air-manure interface (A-MI) mass transfer model. The mass transfer model was developed based on the two-layer film model, where the flux from the bulk liquid phase to the bulk gas phase is related to the molecular exchange of gases between water and gas films (Bajwa et al., 2006; Blunden et al., 2008). A diagram of the two-film model is presented in Figure 2.2. The resistance to the mass transfer of a gas from bulk liquid phase (C_L) to the bulk gas phase (C_a) is from interfacial liquid and gas films. The sum of the liquid (C_{Li}) and gas film (C_{ai}) resistance is termed the overall mass transfer coefficient (K_m). Between the liquid film (C_{Li}) and gas film (C_{ai}) there is a decrease in concentration at the interface. This is explained by Henry's law constant, which relates the equilibrium of a compound from the liquid to the gas phase. By approximating the bulk liquid phase as representing manure, the H_2S flux from the manure is determined using the following equation:

$$J_{H_2S} = K_m\,([H_2S]_{manure} - [H_2S]_{ambient})H_L \qquad (6)$$

where, J_{H_2S} is the H_2S flux (μg m^{-2} min^{-1}), K_m is the overall mass transfer coefficient, $[H_2S]_{manure}$ is the concentration of H_2S in the bulk manure phase, H_L is the Henry's law constant, and $[H_2S]_{ambient}$ is the H_2S gas concentration in ambient air, which is of small magnitude in comparison to $[H_2S]_{manure}$ and can therefore considered to be negligible. Therefore equation (6) can be reduced to:

$$J_{H_2S} = K_m [H_2S]_{manure} H_L \quad (7)$$

2.2.7.1. H_2S Concentration in the Bulk Manure Phase

The concentration of H_2S in the bulk manure phase is determined by:

$$[H_2S]_{manure} = (TSC)\left(f_{H_2S}\right) \quad (8)$$

where TSC is the total sulfide concentration and f_{H_2S} is the fraction of the TSC that is H_2S. Aqueous H_2S exists in equilibrium with the bisulfide anion (HS-) and sulfide anion (S^{2-}). The pH of the liquid constituent determines the dissociation and thus the fraction of the three sulfide species that are available (Snoeyink and Jenkins, 1980). This relationship is shown in Figure 2.3. It can be observed that aqueous H_2S is available from a pH range of ~1-9. Between a pH of 5-9, the fraction of H_2S available decreases as the pH increases due to dissociation into HS^-. Thus the lower the pH, the more H_2S there is available to be transferred from the lagoon into the atmosphere. Therefore f_{H_2S} is determined by the following equation:

$$f_{H_2S} = \frac{10^{-pH}}{10^{-pH} + K_a} \quad (9)$$

where K_a is the dissociation constant.

2.2.7.1.1. Henry's Law Constant

Henry's law quantifies the equilibrium of H_2S at the manure surface interface to the air interface. In this study, a Henry's law constant (H_L) of 0.105 M atm^{-1} for H_2S in water at 25°C was used (Stumm and Morgan, 1996). This Henry's law constant is equal to 0.3893 in dimensionless form (gas concentration/aqueous concentration (g/aq)). Although this Henry's law constant is for water, previous studies suggest that this value can be used for manure. Al-Haddad et al. (1989) evaluated the Henry's law constant for H_2S in distilled water and municipal wastewater with a sulfide concentration of 0.17-0.26 mg L^{-1}. Results showed no significant difference in the Henry's law constant between the distilled water and municipal wastewater. Similarly, in another experiment study, Yongsiri et al. (2005) found there to be little difference in the Henry law constant between de-ionized water and municipal wastewater with a sulfide concentration ranging from 3-8 mg L^{-1}. The similarity of the sulfide levels in both of these studies to the sulfide levels observed in this study (<1-6.4 mg L^{-1}) further support the use of this assumption.

The Henry's law constant is a function of temperature. The effect of manure temperature on the Henry's law constant is taken into account by changes in the standard enthalpy values (Stumm and Morgan, 1996) as described by the Van't Hoff relationship:

$$\ln\left(\frac{H_{L_2}}{H_{L_1}}\right) = -\frac{\Delta H^{\circ}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad (10)$$

where T_1 is 298.15 K (25°C), ΔH^{o} is the enthalpy change, H_{L_1} is the Henry's law constant (g/aq) at 298.15 K, H_{L_2} is the Henry's law constant (g/aq) at temperature T_2, and

R is the universal gas constant (0.008314 kJ mol^{-1} K^{-1}). From this, the following equation was obtained:

$$\log(H_{L_2}) = \log\left(0.39\frac{298.15}{T}\right) - \left\{\frac{19.12}{\ln(10)R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right\} \quad (11)$$

where T is the manure temperature (K). Also included in the equation is a temperature ratio to take into account the conversion of the Henry's law constant. Equation (11) determines that the Henry's law constant increases as manure temperature increases.

2.2.7.1.2. Dissociation Constant

The dissociation constant (K_a) relates the equilibrium between H_2S and HS^- as follows:

$$H_2S_{(aq)} \xleftrightarrow{K_a} HS^-_{(aq)} + H^+ \quad (12)$$

Calculations for the H_2S dissociation in water were made using thermodynamic estimates of standard Gibbs free energy and standard enthalpy. Estimates of these properties at 25°C were obtained from Stumm and Morgan (1996). The standard Gibbs free energy of the H_2S dissociation is used to calculate the dissociation constant at 25°C. The dissociation constant is also a function of temperature, therefore the dissociation constant is also adjusted using the Van't Hoff relationship. From this, the following expression was obtained for the dissociation constant:

$$\log(K_{a_2}) = -6.99 - \left\{\frac{22.15}{\ln(10)R}\left(\frac{1}{T_2} - \frac{1}{298.15}\right)\right\} \quad (13)$$

where K_{a_2} is the dissociation constant at manure temperature T_2 (K). Equation (14) determines that as temperature increases, the H_2S dissociation constant also increases.

In contrast to the Henry's law constant, there is a need to adjust the dissociation constant for the properties of manure. As mentioned, the dissociation constant was calculated based on thermodynamic estimates of H_2S and HS^- in pure water, which does not contain any ions. However, the presence of ions in manure can affect the activity of H_2S and HS^-. Therefore the dissociation constant has to be adjusted for this ion interaction.

This can be achieved by calculating a corrected dissociation constant ($K_a^{'}$) based on the activity coefficients of H_2S ($\gamma\ H_2S_{manure}$) and HS^- ($\gamma\ HS^-_{manure}$), as shown by the following equation (Morel and Hering, 1993):

$$K_a^{'} = K_a \frac{\gamma H_2S_{manure}}{\gamma HS^-_{manure}} \qquad (14)$$

The activity coefficient of a chemical species (x) can be calculated based on it's ion charge (c_x) and the ionic strength of the manure (I), using the Davies equation (Stumm and Morgan, 1996):

$$\log \gamma_x = -0.5(c_x^{\,2})\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right) \qquad (15)$$

where I is a function of electrical conductivity (EC) of the manure as follows (Snoeyink and Jenkins, 1980):

$$I = 0.016(EC) \qquad (16)$$

where the EC of the manure is measured in units of mm hos cm^{-1}. Average electrical

conductivity measurements were obtained from a North Carolina swine anaerobic lagoon liquid characteristics database (Biological & Agricultural Engineering Dept, 1994). The average manure conductivity of 153 samples was 4.612 mm hos cm^{-1}, resulting in an ionic strength of 0.074 mm hos cm^{-1}. H_2S has a zero charge, therefore the resulting activity coefficient ($\gamma\ H_2S_{manure}$) was 1. However HS^- has a charge of -1, giving a HS^- manure activity coefficient ($\gamma\ HS^-_{manure}$) of 0.80. Substituting the activity coefficient values into equation (14), it can be determined that the corrected dissociation constant is ~ 25% larger due to the interaction of HS^- with other ions.

2.2.7.2. Overall Mass Transfer Coefficient

There is limited information available on the mass transfer of H_2S from the manure surface into the gas phase, with only one known study making measurements of the overall H_2S mass transfer coefficient (K_m) from manure with respect to environmental parameters (Arogo et al., 1999). Therefore this study's measurements of the overall H_2S mass transfer coefficient were included in the H_2S manure emission model. A summary of the most important information regarding the overall H_2S mass transfer coefficient are provided here. For more information the reader is referred to the aforementioned paper.

The measurement of the overall H_2S mass transfer coefficient from manure by Arogo et al. (1999) was based on the following equation used to calculate the H_2S concentration in manure at a given time:

$$[H_2S]_{manure} = [H_2S]_0 \exp\left(-\frac{K_m A}{V} t\right) \quad . \quad (17)$$

where $[H_2S]_0$ is the initial H_2S manure concentration, $[H_2S]_{manure}$ is the H_2S manure concentration at time (t), A is the surface area and V is the volume.

In logarithmic form, this equation is presented as:

$$\ln \frac{[H_2S]_{manure}}{[H_2S]_0} = -\frac{K_m A}{V} t \qquad (18)$$

From this equation, K_m can be determined by the slope of $\ln [H_2S]_{manure} / [H_2S]_0$ regression line over time. Measurements were made by placing a convective emission chamber over liquid swine manure containing <1% solids. The chamber dimensions were substituted into equation (18). To examine the influence of environmental parameters on the magnitude of the mass transfer coefficient, Arogo et al. (1999) used a technique known as dimensional analysis. The dimensional analysis considered the following measurable parameters that affect the overall mass transfer coefficient: diffusivity of H_2S in air (D_{H_2S-air}) , air viscosity (μ_{air}), air density (ρ_{air}), surface air velocity (U), air temperature (T_{air}), the liquid manure temperature (T_{manure}) and the characteristic length determining air flow (l). Dimensional analysis of these parameters produced four dimensionless groups, the Sherwood number (Sh), the Reynolds number (Re), the Schmidt number (Sc), and a Temperature ratio (T_r)

$$Sh = C\, Re^n\, Sc^m\, T_r^o \qquad (19)$$

where C, n,m, and o, are constant and exponents that are determined experimentally. The dimensionless groups are defined as:

$$Sh = \frac{K_m l}{D_{H_2S-air}}, \mathrm{Re} = \frac{lU\rho_{air}}{\mu_{air}}, Sc = \frac{\mu_{air}}{\rho_{air} D_{H_2S-air}} \text{ and } T_r = \left(\frac{T_{air}}{T_{manure}} \right) \qquad (20)$$

Arogo et al. (1999) determined ρ_{air}, $\mu_{air,}$ and D_{H_2S-air} using previously published equations. ρ_{air} was calculated as a function of temperature and relative humidity (CRC, 1983-1984), μ_{air} as a function of temperature (CRC, 1983-1984), and D_{H_2S-air} as a function of pressure, temperature, and molecular characteristics (Fuller et al., 1966). The constant (C) and the exponents n and o were determined by varying the manure temperature from 15-35^{o}C and the air velocity from 0.1-0.5 ms^{-1}, while keeping the other variables constant. The values of C, n, and o were determined to be 58.60, -0.13 and -1.62, respectively. However, exponent m could not be determined using the same methodology. Therefore Arogo et al. (1999) determined two separate m components based on theoretical considerations, one representing the diffusivity, the other representing the viscosity of air and the density of air. The diffusivity exponent was determined as 0.58, based on available literature. The viscosity and density of air exponent was calculated as 0.43, using the relationship between the Schmidt number and the Sherwood number. The constant and exponent values were substituted into equation 20. From this, equation 20 was rearranged to express the overall mass coefficient in terms of environmental and system parameters:

$$K_m = 58.60 \frac{\mu_{air}^{0.56} T_{manure}^{1.62} D^{0.58}}{U^{0.13} l^{1.13} \rho_{air}^{0.56} T_{air}^{1.62}} \quad (21)$$

The characteristic length (l) for the system was the diameter of the chamber, which was 0.46 m. In this study, wind speed measurements were made at a height of 10

m. Therefore to determine surface air velocity, a power law profile, which is commonly used in air pollution studies was applied (Arya, 1999).

$$\frac{V}{V_r} = \left(\frac{z}{z_r} \right)^m \tag{22}$$

where V_r is the wind velocity at the reference height Z_r , which is 10m. Surface wind velocity (V) was calculated for a height of 0.1m. The value of exponent m is determined as 0.15 for water surfaces (Arya, 1999).

2.3. RESULTS AND DISCUSSION

2.3.1. Lagoon Flux

2.*3.1.1. Seasonal Fluxes*

Seasonal H_2S lagoon fluxes and their corresponding environmental parameters are summarized in Table 2.1.

Of the four seasons, the H_2S flux was highest during the summer season with an average flux value of 3.82 μg m^{-2} min^{-1}. The 2nd highest flux was measured in the fall season with a value of 1.26 μg m^{-2} min^{-1}. The lowest fluxes were in the spring and winter, 0.27 and 0.08 μg H_2S m^{-2} min^{-1} respectively. Both lagoon and air temperature seasonal averages were representative of seasonal trends. The seasonal pH averages varied, with the lowest pH occurring in the summer (7.26). The pH was higher in the fall season with a value of 7.52. The highest seasonal pH averages were in the winter and spring with values of 8.02 and 8.03, respectively. Wind speed seasonal averages ranged from 1.38-2.76 ms^{-1}, with the lowest seasonal average occurring in the summer and the highest in

the spring. Average seasonal sulfide concentrations were hard to determine, as ~ two-thirds of the samples analyzed had a sulfide content below the analytical instruments limit of detection of 1 mg L^{-1}. The averages presented are the maximum possible average of sulfide concentration, assuming that the sulfide samples concentrations are at the detection limit, therefore equaling 1 mg L^{-1}. It can be observed from Table 2.1 that the environmental parameters often have less 15 minute average data points than the corresponding seasonal lagoon flux. This is the result of the instruments not working correctly at various times during the experimental study.

H_2S swine CAFO lagoon fluxes have been determined by other studies around the U.S. A summary of the H_2S lagoon fluxes and corresponding environmental parameters are presented in Table 2.2. It can be observed that this study's H_2S fluxes are similar to measurements reported by Blunden and Aneja, (2008) at the same sampling site. Both studies have their highest fluxes in the summer and their lowest in the winter. For the fall sampling season, the flux is higher in this study than in comparison to Blunden and Aneja, (2008). Conversely in the spring season, Blunden and Aneja, (2008) reported flux is slightly higher. In comparison to other swine CAFO studies in the U.S., the fluxes are generally 2-3 orders of magnitude lower, apart from two of Byler et al. (2004) study seasons, where they report an H_2S flux of 4.2 and 19.2 μg m^{-2} min^{-1}, respectively. A possible reason for higher fluxes in the other studies is the sulfide content. Zahn et al. (2001) sulfide concentration is considerably higher than those reported by Blunden and Aneja, (2008), and an order of magnitude higher than those reported in this study. This parameter may account

for the differences in fluxes between the studies, however there is no sulfide concentration reported in Lim et al. (2003) and Byler et al. (2004) studies.

It can be observed that the seasonal pH values in the summer (7.26) and fall (7.52) are lower than the seasonal pH values reported by Blunden and Aneja, (2008), which range from 8.0-8.1. These seasonal pH values are also lower than other previous studies that have reported H_2S fluxes from swine CAFO lagoons (Table 2.2), apart from one study by Byler et al. (2004), which measured a pH of 7.4. A comparison of this studies' pH values to other reported pH values from swine CAFO lagoons in North Carolina is presented in Table 2.3.

As mentioned, summer and fall seasonal pH values are lower than those observed by Blunden and Aneja (2008) at the same sampling site. However, they are within the range of values reported by Aneja et al. (2000). Aneja et al. (2000) made continuous measurements of pH for 1-2 weeks in four different seasonal periods. The lowest seasonal pH was summer with an average value of 7.5 and a range of 7.1-7.8. In comparison, the fall seasonal pH in this study was similar with a value of 7.52. The summer seasonal pH (7.26) was slightly lower, however it is within the range of Aneja et al. (2000) reported summer pH values. Bicudo et al. (1999) also measured the pH of swine CAFO lagoons in North Carolina. Bicudo et al. (1999) made measurements of lagoon characteristics including pH in 15 different lagoons in North Carolina. Samples were collected approximately once a month for a two year period. Results showed the mean lagoon pH for the 15 lagoons to range from 7.6-8.0, which is higher than the pH values reported in the fall and summer seasons from this study. In addition, a North Carolina lagoon database (Biological & Agricultural Engineering, 1994) has made a number of measurements of lagoon pH from different

lagoons. This database reports an average pH of 7.8 from 179 lagoon samples, which is also higher than the summer and fall pH values reported in this study. However, the summer and fall pH values are within the range of pH observations in this database, which was 7.0-8.5. It should be noted that for the Biological & Agricultural Engineering, (1994) database, that the number of different lagoons sampled from is not specified.

The seasonal pH standard deviations in this study range from 0.10-0.14 (Table 2.3), which is slightly higher than those observed by Blunden and Aneja (2008). However, they are of similar magnitude to seasonal pH standard deviations observed by Aneja et al. (2000). It can also be observed that the ranges of pH observed in this study are larger than those reported by Blunden and Aneja (2008). They are though similar for three of the four seasons to those reported by Aneja et al. (2000). The exception is the winter season, where there is a large pH range of 7.27-8.25. However, it should be noted that large range is the result of low pH values on one particular evening and nighttime. If this data is excluded from analysis, then the lowest pH value would be 7.86. The cause of this low pH event is unknown.

2.*3.1.2. Diurnal Trends*

The diurnal trends of seasonal H_2S emissions are shown in Figures 2.4a, and 2.4b. It should be noted that for the diurnal trend analysis and analysis thereafter that H_2S emissions caused by 'bubble transport' mechanisms have been omitted. In the summer season (Figure 2.4a.), it can be observed that the fluxes increase during the nighttime and early morning hours, resulting in the summer flux peaking at 10:00 with a value of 4.21 $\mu g\ m^{-2}\ min^{-1}$. During the afternoon and evening the flux decreases reaching a minimum of 1.53 $\mu g\ m^{-2}\ min^{-1}$ at 18:00. The fall diurnal flux trend (Figure 2.4a.) is similar to the

summer season, with fluxes increasing during the nighttime and early morning, and then decreasing in the afternoon and evening. The fall season has a maximum hourly flux at 6:00 with a value of 1.11 μg m^{-2} min^{-1} and a minimum hourly flux of 0.58 μg m^{-2} min^{-1} at 21:00. In comparison, the winter and spring seasons showed different diurnal trends (2.4b.). In the spring, the flux generally increases during the nighttime, morning and afternoon, reaching a peak of 0.13 μg m^{-2} min^{-1} at 15:00. In the evening fluxes mostly decrease reaching a minimum of 0.05 μg m^{-2} min^{-1} at 23:00. For the winter diurnal trend, fluxes increase during the morning, afternoon and evening reaching a maximum of 0.11 μg m^{-2} min^{-1} at 20:00. The flux trend decreases throughout the nighttime reaching a minimum of 0.04 μg m^{-2} min^{-1} at 7:00.

2.3.1.3. The Influence of Environmental Parameters on H_2S Lagoon Flux

Lagoon pH affects H_2S flux from lagoons, as is discussed in the modeling section of this paper. Anaerobic lagoon pH usually ranges from 7-8.5. In this region the fraction of H_2S available increases as the pH decreases (Figure 2.3.). Therefore it is expected that as pH decreases, that H_2S fluxes will increase.

A comparison of average seasonal flux and pH values support the influence of pH on emissions (Table 2.1), with higher seasonal fluxes corresponding with lower seasonal pH values. The effect of pH was further investigated by examining it's seasonal diurnal trend (Figure 2.5.). It can be observed that during the daytime that pH decreases in the winter and spring seasons, which corresponds to when H_2S fluxes are at their highest (Figure 2.4b.). In the summer and the fall the pH increases during the daytime. The summer diurnal trend does show a sharp decrease from 13:00-14:00, but this is the result

of a lack of data collection at this hour, as daily experimental duties were often carried out at this time. The daytime pH increases correspond with H_2S fluxes decreases during the summer and fall sampling seasons (Figure 2.4a.).

Further analysis of the influence of pH and other environmental parameters on H_2S flux were performed using statistical analysis. For the statistical analysis, 15 minute averaged data points were used. H_2S fluxes had a lognormal distribution, therefore fluxes were log transformed. The relationship between H_2S flux and environmental parameters were determined by using the coefficient of determination (r^2). These r^2 values and their respective p-values are presented in Table 2.4. It should be noted that the variance in the number of 15 minute data points is the result of the instruments occasionally not working properly during the sampling periods. In addition to lagoon pH and lagoon temperature, air temperature was also included in this analysis, as the effect of the dynamic-flow through chamber system on air temperature has found to be small. Arkinson (2003) using this system for flux measurements found the difference in air temperature inside and outside of the chamber to be 1.55 ±2.30^oC.

Of the environmental parameters, pH had the strongest correlation with H_2S flux (r^2 (log H_2S flux) = 0.74; $p<0.0001$). This relationship is presented in Figure 2.6a. This high r^2 value supports the patterns observed between H_2S flux and pH diurnal trends. Lagoon temperature had the 2nd strongest correlation with H_2S flux (r^2 (log H_2S flux) = 0.44; $p<0.0001$). This relationship is presented in Figure 2.6b. The effect of lagoon temperature on H_2S flux is related to changes in the mass transfer coefficient. As lagoon temperature increases, the mass transfer of H_2S increases across the air-manure interface,

thus increasing H_2S fluxes (Arogo et al., 1999). Additionally, an increase in lagoon temperature can increase microbial activity and therefore increase rates of decomposition. This can result in more sulfide being available. Ambient air temperature was also found to have a significant relationship with H_2S flux (r^2 (log H_2S flux) = 0.33; <0.0001). Similarly to the effect of lagoon temperature, increases in air temperature can increase the mass transfer coefficient and therefore H_2S fluxes. As mentioned, ~two-thirds of the lagoon samples collected had a sulfide content below the analytical detection limit of 1 mg L^{-1}. Therefore the data set was too limited to perform accurate statistical analysis.

Further statistical analysis was conducted to confirm the effect of environmental parameters and to develop a statistical observational model. Statistical analysis was performed using SAS (Statistical analysis software v8, Cary, NC). As mentioned, H_2S data was collected continuously as 15 min averages, therefore each data point is not necessarily independent of each other. As a result, when performing multiple linear regression, autocorrelation was taken into account. Therefore the H_2S statistical observational model was determined using autoregression and Yule-Walker estimates. Parameters were deemed significant if their p-value was < 0.05. Using this statistical technique, the best-fitting model was the following:

$$\text{Log } H_2S \text{ flux} = 4.5003 - 0.7573(\text{pH}) + 0.0262\,(L_T) + 0.0202(A_T) \quad (23)$$

where log H_2S flux is in units of $\mu g\ m^{-2}\ min^{-1}$, pH is unitless, and L_T is the lagoon temperature in ^oC and A_T is the air temperature in ^oC. The statistical observation model had an r^2 value of 0.68 ($p < 0.0001$) (Figure 2.7.) In this model, pH is by far the most dominant environmental parameter, increasing H_2S lagoon emissions as it decreases.

Lagoon temperature had the second largest influence on H_2S flux, increasing H_2S lagoon fluxes as it increases. However, this influence was a lot weaker than that of pH. Ambient air temperature has the smallest influence of the environmental parameters. Similarly to lagoon temperature, H_2S emissions increases as air temperature increased.

2.3.2. Barn Concentrations and Emissions

2.*3.2.1. Seasonal Concentrations and Emissions*

The average seasonal H_2S barn concentrations and emissions, as well as ventilation rates, and the environmental parameters, barn temperature and ambient temperature are presented in Table 2.5.

Average seasonal ambient temperatures range from 8.4^{o}C in fall to 26.0^{o}C in summer. The winter sampling season was warmer than normal and therefore had a higher average ambient temperature than the fall with a value of 11.3^{o}C. Higher ambient temperatures increase the temperature inside the barn. Over the four sampling seasons, the r^2 value for ambient temperature and barn temperature was 0.89 ($p<0.0001$). However, the seasonal averages between these two parameters do not show the same trend. The winter season has an average ambient temperature 2.8 ^{o}C higher than the fall season, whereas the seasonal winter barn temperature is 1.6 ^{o}C less than in the fall. The reason for this is unknown, however it is suggested that it could be the result of the number of animals in the barn. In the winter sampling season, there were almost half the amount of pigs (476) compared to the fall season (994.5). This was the result of sampling being conducted later in the rotation, and therefore some of the pigs had been sold. It is

hypothesized that the lower pig numbers in the winter, resulted in less body heat production and thus lower barn temperatures.

Ventilation rates are influenced by ambient temperature, and thus barn temperature. As barn temperature increases, more fans turn on, resulting in increased ventilation rates. In this study over the four sampling seasons, barn temperature and ventilation rate have an r^2 value of 0.58 ($p<0.0001$). The main reason this relationship is not stronger is because increases in ventilation rate are not proportional to increasing barn temperature, as ventilation fans only turn on when a certain temperature is reached. A further reason is that there may have been differences in the temperature measured at the barn fan in comparison to the fan controller. The average seasonal ventilation rates corresponded with average seasonal barn temperatures. Ventilation rates varied from 269 $m^3\ min^{-1}$ in the winter to 1763 $m^3\ min^{-1}$ in the summer.

The highest average seasonal concentration occurred in the spring sampling season, which was 631 ppb. However, this average is not a true value as 173 of the 649 (~ 27%) 15 minute averaged H_2S concentration data points had concentrations above the maximum range of the H_2S analyzer (1000 ppb). Therefore the actual average concentration is higher than the reported value. The reader should take this into account when spring concentration and emission values are described in comparison to others.

The spring average seasonal concentration was almost twice as high as the next highest average seasonal concentration, which was 327 ppb for the fall season. The two lowest average concentrations occurred in the winter and summer seasons, 163 and 72 ppb, respectively. H_2S concentration is expected to be influenced by ventilation rate. This

relationship was investigated by using the coefficient of determination (r^2). Over all four sampling seasons, the distribution of H_2S concentration was lognormal, therefore H_2S concentration was log transformed. Log H_2S concentration was found to have a fairly strong negative relationship with ventilation rate (r^2=0.45, $p<0.0001$).

The highest H_2S emissions occurred in the spring season with a value of 647 g day^{-1}. The next highest were the fall and summer seasons, 206 and 189 g day^{-1}, respectively. The lowest emission was during the winter with a value of 79 g day^{-1}.

Total animal weight is considered to be one of the largest factors influencing emissions from a barn. Emissions were therefore normalized by 500 kg of live animal weight (LAW), also known as 1 animal unit (AU). The calculated live animal weight, the corresponding pig production data and the normalized H_2S emissions are shown in Table 2.6. The weight of the pigs was based on their initial weight entering the swine CAFO, which ranged from 20-24 kg. It was then assumed that the pigs gained weight at a rate of 5.125 kg per week. Mortality rate was recorded and taken into account when calculating pig numbers.

After taking into account the total animal weight, there is still considerable variance in the emission rate. The highest seasonal H_2S normalized emission rate occurs in the spring with an emission of 7.31 g day^{-1} AU^{-1}. The next highest is the fall season with an emission of 2.99 g day^{-1} AU^{-1}, followed by the summer season with an emission of 2.20 g day^{-1} AU^{-1}. The lowest normalized emission rate was in the winter with an emission of 0.71 g day^{-1} AU^{-1}.

Table 2.7 presents the concentrations and emissions of H_2S from other swine finishing CAFO studies. Studies have been selected that report emissions normalized for live animal weight or that can be calculated based on information provided in the paper. These studies were mainly conducted in the mid-western part of the U.S., apart from the Blunden et al. (2008) study, which was conducted at the same sampling site in North Carolina and also a study from South Korea. Average daily mean (ADM) concentrations for this study ranged from 73-645 ppb. The highest ADM concentration (645 ppb) occurred in the spring season, which was higher than the corresponding seasonal ADM concentration in the Blunden et al. (2008) study (441 ppb). This concentration is also higher than those reported in other swine CAFO finishing studies. As previously mentioned, the spring ADM concentration is actually higher than this, due to 27% of the 15 minute average concentrations being above the analyzer's limit of detection. The 2nd highest ADM concentration was in the fall with a concentration of 307 ppb. This was only slightly higher than Blunden et al. (2008) corresponding seasonal ADM concentration of 304 ppb. The winter season had the next highest ADM seasonal concentration (150 ppb). This concentration was considerably lower than Blunden et al. (2008) winter ADM concentration, which was their study's highest ADM seasonal concentration with a value of 632 ppb. The lowest ADM season concentration was in the summer with an average of 72ppb. Similarly, Blunden et al. (2008) lowest concentration also occurred in the summer with a value of 47 ppb. These lowest average seasonal concentrations are significantly higher than those reported by Jacobson et al. (2003). They made measurements from a finishing swine CAFO and calculated average

concentrations of 10.1 and 8.7 ppb for the winter and summer, respectively. However this swine CAFO employs a deep bedded manure collection system. In comparison to the other previous studies, the ADM concentrations are of a similar magnitude, despite the differences in management and environmental conditions.

Normalized emission rates in this study range from 0.71-7.31 g day^{-1} AU^{-1}. These compare well with the normalized emissions reported by Blunden et al. (2008) at the same sampling site, which ranged from 1.2-4.2 g day^{-1} AU^{-1}. However, there is some variance in seasonal trends. The lowest seasonal emission in this study occurs in the winter (0.72 g day^{-1} AU^{-1}). In comparison, Blunden et al. (2008) report their highest seasonal emission in the winter sampling season (4.2 g day^{-1} AU^{-1}). The reason for this seasonal difference could be due to ventilation patterns. In this study, 54% of the winter season data was collected with the 1^{st} fan going on and off intermittently. It is hypothesized that when the fan is off, the air flow pattern of the barn changes, resulting in less air, and thus less H_2S being drawn from the shallow manure pit, causing lower H_2S barn concentrations and emissions. Other possible reasons for the difference include the effect of live animal weight, which may not be linear. If so, this could have a particularly strong effect on winter emissions, as this season has the largest live animal weight (Tables 2.5 and 2.6). Furthermore there could be an effect in emissions related to pig numbers and pig weight. In all eight sampling seasons conducted between the two studies, the winter season in this study has the heaviest pigs, but the fewest numbers, with ~50% less than all the other sampling seasons. There is also variance in the spring season emissions. In this study, a spring normalized emission rate of 7.31g day^{-1} AU^{-1} was

calculated, compared to 3.3 g day^{-1} AU^{-1} reported by Blunden et al. (2008). The reason for this difference is not known. The summer and fall seasons compare well, with the emissions for both seasons in this study only slightly higher than the corresponding season in the Blunden et al. (2008) study, 2.20 g day^{-1} AU^{-1} compared to 1.2 g day^{-1} AU^{-1} in the summer, and 2.99 compared to 1.7 g day^{-1} AU^{-1} in the fall.

The swine CAFO emissions in North Carolina are of a similar magnitude to other swine CAFO studies, which range from 0.11-8.5 g H_2S day^{-1} AU^{-1} (Table 2.6). The variance in emissions observed in Table 2.6 occurs as a result of different production, management and environmental conditions. Production factors include the number and weight of the pigs. Management factors can be divided into two subtypes, manure management and housing management. Manure management factors include depth and characteristics of storage pit, waste storage time, flushing frequency, and length of time since the house has been cleaned. Housing management factors include barn size, barn structure and characteristics and ventilation type. Environmental factors include manure temperature, manure pH, and air velocity above the manure. Additionally, the type of measurement methodology used could effect reported emissions, particularly for barns with natural ventilation, where flow rate can be difficult to measure.

Despite the influence of these various factors, there are still some trends that can be observed in swine CAFO H_2S emission studies. There are four studies, including this study that report emissions across a range of seasons (Jacobson et al., 2003; Heber et al., 2000; Blunden et al., 2008). In this study, the Jacobson et al. (2003) and Heber et al. (2000) studies, the winter seasonal emission rate is the lowest. The only study that does

not show this is Blunden et al. (2008). This suggests that temperature may play a role in influencing emissions.

A further observation is that the emissions tend to be higher, the longer the waste is stored. From the U.S studies, there are four seasonal emissions reported for the deep pit manure management system (Heber et al. 1997; Ni et al. 2002; Zhu et al. 2000), which typically flush their pits after a pig rotation, which can be several months. The average of these emissions is 3.6 g day^{-1} AU^{-1}. The four seasonal emissions are from summer, winter and fall twice. Therefore the averaged emissions may be considered representative of a year. This emission average is slightly higher than the average emissions from two years of measurement data (this study and Blunden et al., 2008) from a weekly flushed pit in North Carolina, which is 3.0 g day^{-1} AU^{-1}. In turn, the average weekly flushed emissions are higher than the average emissions measured over a year from a daily flushed facility, which is 0.83 g day^{-1} AU^{-1} (Heber et al., 2004). However, the lowest emissions are reported for a deep bedded manure management system. A deep bedded system places a layer of straw or sawdust on the barn floor surface. Jacobson et al. (2003) reports emissions of 0.11 and 0.16 g day^{-1} AU^{-1} for the winter and summer sampling seasons, respectively. In this study the waste removal frequency is not reported.

It is unknown why the deep bedded system has lower emissions. However, it may be the result of high manure temperatures and thus evaporation, reducing the amount of manure (Groenestein and Van Faassen, 1996). In addition, the organic content of the bedding material may influence H_2S emissions. Andersson, (1996) reported that the organic content of the bedding material can influence ammonia emissions, by causing

changes in the biochemical cycling of nitrogen in the manure. However the extent of a similar effect on the biochemical cycling of sulfur in manure is unknown.

Similar manure management trends are reported by a study in South Korea by Kim et al. (2008). They measured H_2S emissions from five barns. Two of the barns employed a deep pit system. A further two had a scraper removal system, where manure could be removed several times a day. One barn had a deep bedded system, which was cleaned once a month. Deep pit systems had the highest average emission rate, with an emission of 7.6 g day^{-1} AU^{-1}. The scraper removal system had a lower average emission with a value of 6.1 g day^{-1} AU^{-1}. The lowest emission was measured in the deep bedded system with an emission of 3.0 g day^{-1} AU^{-1}.

2.3.2.2. Diurnal variation of H_2S Emissions, Concentrations and Ventilation rates

The calculated H_2S emissions are the product of concentration and ventilation rate; therefore when discussing the diurnal trends of H_2S emissions it is also necessary to consider the diurnal trends of concentration and ventilation rate. The seasonal diurnal trends for H_2S emissions and the corresponding seasonal diurnal trends for H_2S concentration and ventilation rate are shown in Figures 2.7-2.10.

The summer H_2S diurnal emission trend (Figure 2.8a) shows two peaks, one at 6:00 and another at 18:00. The early morning peak has an emission rate of 2.84 g day^{-1} AU^{-1}, which is the highest hourly emission rate. The evening peak emission rate is slightly lower with a value of 2.57 g day^{-1} AU^{-1}. The diurnal trend also shows two troughs, one at midday, and another at 22:00. The nighttime trough is slightly lower than the midday trough, with an emission rate of 1.77 g day^{-1} AU^{-1} compared to of 1.80 g day^{-1}

AU^{-1}. The diurnal emission trend can be explained by examining the concentration and ventilation rate diurnal trends (Figure 2.8b). The ventilation rate is as expected, increasing during the day as barn temperatures rise, reaching a maximum hourly emission of 2417 m^3 min^{-1} at 10:00, and decreasing during the evening and night as barn temperatures decrease, resulting in a minimum hourly ventilation rate of 883 m^3 min^{-1} at 5:00. The relationship between ventilation rate and concentration is expected to be inverse, however it can be observed that there are two concentration peaks that are independent from ventilation rate. These concentration peaks correspond with the emission peaks. The smaller of the two peaks spans across the afternoon and evening, where the concentration increases from the minimum hourly emission rate of ~35 ppb at 13:00 to ~56 ppb at 19:00. In the corresponding time period, the ventilation rates slightly decrease from ~2400 m^3 min^{-1} to ~2230 m^3 min^{-1}. However, it is hypothesized that the influence of barn temperature, which is highest in the afternoon, may also contribute to the peak. Increases in barn temperature will increase the manure temperature. Similarly to lagoon emissions, the higher manure temperature will result in enhanced emissions due to effect of temperature on two different processes. Firstly, the higher temperatures lead to increased rates of decomposition, resulting in more sulfide being available. Secondly, an increase in temperature will increase the mass transfer of H_2S across the air-manure interface (Arogo et al., 1999).

The other emission peak which occurs at 6:00 is likely the result of different factors. Examination of the ventilation rate between 2:00 and 6:00, shows a relatively constant ventilation rate at around 900 m^3 min^{-1}. However during the same time period,

the concentration increases from ~115 ppb to a maximum hourly concentration of ~155 ppb. This increase though is not due to increasing barn temperature, as barn temperature is decreasing during this time period. Therefore this concentration increase is likely the result of a 'build up effect'. Although the barn temperatures are decreasing throughout the night, the summer barn temperatures are still high (25.0-25.5^{o}C), resulting in significant emissions. However, due to the configuration of the ventilation system, a maximum of only two fans are running at this time. Therefore during these hours there is more H_2S being produced inside the barn than leaving the barn through ventilation. Therefore over time, H_2S accumulates or builds up inside the barn, resulting in the emission peak from 5:00-7:00. As morning continues, barn temperatures increase, triggering more fans to come on. This causes a rapid decrease in concentration until 9:00. From 9:00-13:00 the concentration is at it's lowest, fluctuating between ~35-43 ppb.

The fall diurnal H_2S emission trend (Figure 2.9a) has a daytime peak between 13:00-18:00. During this period the emission rates are above 4.0 g day^{-1} AU^{-1}, with a highest average hourly emission of 4.67 g day^{-1} AU^{-1} at 14:00. In the evening, night and early morning (19:00-6:00), the emissions slowly decrease reaching a minimum hourly emission rate of 2.18 g day^{-1} AU^{-1} at 6:00. Between 6:00 and 7:00 there is a rapid increase in emission rate to 2.85 g day^{-1} AU^{-1}. For the remainder of the morning, the emission is reasonably steady at ~ 3.0 g day^{-1} AU^{-1}.

Examination of the concentration and ventilation rate diurnal trends (Figure 2.8b) show an approximate inverse relationship. Between 19:00 and 4:00, the ventilation rate slowly decreases from ~ 310 m^3 min^{-1} to a minimum hourly average of 221 m^3 min^{-1}.

Between 4:00 and 6:00 the ventilation rate is stable, ranging between 221-222 m^3 min. Correspondingly between 19:00 and 6:00, the H_2S concentration is fairly constant ranging from ~330 ppb to ~365 ppb. The relationship between the concentration and ventilation rate results in the slight decrease of emissions between 19:00 and 6:00.

Ventilation rates increase from 6:00-14:00 during the daytime, reaching a maximum average hourly peak of 666 m^3 min^{-1} at 14:00. At 15:00 the ventilation rate is only slightly lower with an hourly average of 642 m^3 min^{-1}. After this there is a rapid decrease in ventilation rates until 19:00. As ventilation rates increases during the morning, the concentration correspondingly decreases until 11:00. However, from 11:00-15:00, the concentration levels stop decreasing. Instead they are fairly steady with a slight fluctuation that results in a minimum hourly concentration of ~237 ppb at 15:00. It is during this time period that H_2S emissions start to increase. Similarly to summer, it is proposed that higher afternoon barn temperatures increase the emission of H_2S inside the barn. This keeps the concentration levels steady as described and then increase the concentration as the afternoon continues, resulting in a maximum hourly concentration of 371 ppb at 18:00. This effect results in the daytime emission rate peak between 13:00-18:00.

The average hourly winter emission trend (Figure 2.10a) is highest in the morning and afternoon between 9:00 and 17:00, ranging from 0.81 g day^{-1} AU^{-1} to a maximum hourly emission rate of 1.49 g day^{-1} AU^{-1} at 15:00. After 17:00, emissions decrease, before fluctuating into the late evening, reaching a minimum hourly emission rate of 0.47

g day^{-1} AU^{-1} at 22:00. For the remainder of the night and early morning (23:00-8:00), the emission rate is fairly constant, ranging from 0.48-0.59 g day^{-1} AU^{-1}.

The ventilation rate diurnal trend (Figure 2.10b) is as expected, with ventilation rates generally increasing during the morning and early afternoon and decreasing during late afternoon, evening and nighttime. The highest ventilation rates occurred between the hours of 11:00-17:00, ranging from 397 m^3 min^{-1} to a maximum hourly emission rate of 529 m^3 min^{-1} at 15:00. During the evening, nighttime, and morning (18:00-10:00), the ventilation rates were all less than 300 m^3 min^{-1}, with a minimum emission rate of 162 m^3 min^{-1} at 6:00. The winter diurnal concentration trend is different from the other seasons as it is fairly constant with slight fluctuations (Figure 2.10b). The maximum hourly concentration occurs at 6:00 with a value of 183 ppb. The minimum hourly concentration is 150 ppb, which occurs at 14:00. In the winter season, concentration does not show a strong inverse relationship with ventilation rate. When ventilation rates are at their highest between 11:00-17:00, the average ventilation rate is 427 m^3 min^{-1} and the average concentration is 161 ppb. However, for the time between 18:00-10:00, when ventilation rates are significantly lower with an average ventilation rate of 205 m^3 min^{-1}, the average concentration is only slightly higher with a value of 167 ppb. A possible reason for the weak relationship between the diurnal trends of concentration and ventilation rate is related to ventilation patterns. This factor was also discussed as a possible reason for low overall winter emissions. In the winter sampling season, 274 out of 507 (54%) 15 minute data points were collected with the 1st fan going on and off intermittently, with 258 of the 274 (94%) data points occurring during the evening, night, and morning between 18:00-

10:00. As mentioned, it is hypothesized that when the fan is off, the air flow pattern of the barn changes, resulting in less air moving across the manure surface, and thus less H_2S being drawn from the manure surface. It is suggested that this factor has resulted in low evening, nighttime and early morning concentrations.

The spring diurnal emission trend (Figure 2.11a) is highest between 14:00-18:00 with a maximum hourly emission rate of 11.17 g day^{-1} AU^{-1} at 17:00. After 17:00, the emission rate decreases throughout the evening to an emission rate of 6.46 g day^{-1} AU^{-1} at 1:00. From 1:00-8:00, the emission rate is fairly steady ranging from 6.40-6.61 g day^{-1} AU^{-1}. At 9:00 the emission rate starts to decrease reaching a minimum hourly emission rate of 5.48 g day^{-1} AU^{-1} at 11:00. However, the evening, nighttime and early morning hourly values may not reflect the actual emission rate. As mentioned, 173 out of 649 (~ 27%) 15 minute averaged H_2S concentration data points had concentrations above the maximum range (1000 ppb) of the H_2S analyzer. 157 of these 173 (~88%) data points occurred at nighttime between 22:00 and 9:00 on four of the seven sampling days. The other data points that exceeded the detection limit occurred earlier in the evening on two of these four days at 17:30 and 20:15, respectively.

The ventilation diurnal trend (Figure 2.11b) starts to increase at 7:00 reaching a maximum hourly rate at 12:00 of 1135 m^3 min^{-1}. During the same time period, the concentration trend (Figure 2.11b) decreases rapidly from 735 ppb to a minimum of 237 ppb at midday. This decreasing concentration trend causes the hourly emission minimum. From 12:00-17:00, the ventilation rate has a slight decreasing trend, reaching a ventilation rate of 998 m^3 min^{-1}. During the same time period, concentration almost

doubles, increasing to an hourly concentration of 532 ppb at 17:00. This concentration increase coincides with the daytime emission peak. Similarly to other seasons, it is hypothesized that this is the result of increasing barn temperature. In the evening there is a large decrease in ventilation rate. However, the corresponding concentration continues to increases at a similar rate to the afternoon. This results in the emission rate decrease. The ventilation rate continues to decrease until 1:00 reaching an hourly value of 359 m^3 min^{-1}. Between 2:00 and 6:00 the ventilation rate is relatively constant, ranging from a minimum hourly value of 357 m^3 min^{-1} at 5:00 to 376 m^3 min^{-1}. As mentioned, at ~22:00 the quality of the concentration data starts to decrease. There are three complete nighttime profiles and one partial profile, where the detection limit is not exceeded. In all of the profiles, the ventilation rates remain relatively constant throughout the evening and night. However, there is variance in the concentration profiles. Two of the complete profiles concentrations increase through the evening and night, the other remains fairly constant. The partial profile shows a decrease in concentration through the evening and night. The difference in profile trends mean that it is difficult to determine the spring seasonal nighttime trend.

2.3.2.3. *The Influence of Barn Temperature on Barn Emissions*

Barn temperature is an important environmental parameter that can influence H_2S emissions from barns. As mentioned, increases in barn temperature can increase emissions. Observational analysis of diurnal trends of emissions, concentrations and ventilation rates suggested that barn temperature could be a significant factor in influencing emissions.

The effects of barn temperature on normalized H_2S emissions were investigated using regression analysis. Spring data points with concentrations above the concentration detection limit were excluded from the regression analysis. Normalized H_2S emissions had a lognormal distribution, therefore emissions were log transformed. Log H_2S emissions were found to have a weak positive relationship with barn temperature, with an r^2 value of 0.19 ($p< 0.0001$) (Figure 2.12).

A major reason that the relationship between H_2S barn emissions and barn temperature is not stronger is that the barn is a dynamic environment. The amount of H_2S in the barn at a certain moment is a function of H_2S input, which is the amount of H_2S being produced by the manure, and H_2S output, which is the amount of H_2S leaving the barn through ventilation. The amount of H_2S produced by the manure is influenced by environmental factors, whereas the amount of H_2S leaving the barn is determined by ventilation rate. The balance between the inputs and the outputs is constantly changing over time. Therefore, it is hard to determine the extent of the influence of environmental parameters, such as barn temperature in this study.

There are other environmental and microbial parameters, which may influence barn emissions, e.g. manure pH. However, it was beyond the scope of this study to measure other environmental and microbial parameters.

2.3.3. Modeling of H_2S Manure Emissions

2.3.3.1. Sensitivity Analysis of Air-Manure Interface Mass Transfer Model

To assess the effect of environmental parameters on the air-manure interface (A-MI) mass transfer model predicted flux values, a sensitivity analysis was performed. This was achieved by holding all environmental parameters constant, while varying the environmental parameter of interest. The constant values used were the average of the four seasonal average values. These were as follows: 1.52 mg L^{-1} for total sulfide concentration, 19.6 ^{o}C for lagoon temperature, 7.71 for pH, 15.3 ^{o}C for ambient air temperature and 1.97 ms^{-1} for wind speed at a height of 10m. Figures 2.13-2.15 present the sensitivity analysis of H_2S emissions with respect to different environmental parameters.

The sulfide concentration sensitivity analysis showed H_2S fluxes to increase linearly as total sulfide concentrations increase (Figure 2.13a). As expected, the pH sensitivity analysis shows a different trend, with H_2S fluxes decreasing with increasing pH (Figure 2.13b). This trend is similar to the effect of pH on the fraction of H_2S available as presented in Figure 2.3. The lagoon temperature sensitivity analysis shows H_2S fluxes to slightly increase, with increasing lagoon temperature (Figure 2.14a). Higher lagoon temperatures increase predicted fluxes as a result of the lagoon temperature increasing the mass transfer of H_2S across the air-manure interface. Additionally increases in lagoon temperature also increase the Henry's law constant, which also results in higher H_2S fluxes. However, the effect of lagoon temperature on H_2S flux is reduced due to the influence of lagoon temperature on dissociation rate. Higher lagoon

temperatures increase the dissociation rate of H_2S, resulting in a smaller fraction of H_2S available.

To allow a sensitivity analysis of ambient air temperature, the density of moist air was assumed to be constant. This constant value was obtained by using the average of the seasonal moist air density values. The sensitivity analysis shows that as air temperature increases, predicted H_2S flux very slightly decreases (Figure 2.14b). This is expected, as in the model, air temperature is only used in calculating the overall mass transport coefficient, where it is a denominator in the relevant equation (Equation 21).

The sensitivity analysis of wind speed showed predicted H_2S flux to decrease with increasing wind speed at 10 m (Figure 2.15). However this decrease is most rapid at low wind speeds. As wind speeds increase, the rate of decrease gets smaller, which results in fairly constant predicted H_2S fluxes for higher wind speeds. The wind speed trend is related to the overall mass transfer coefficient, developed by Arogo et al. (1999). However, there are some limitations associated with the use of Arogo et al. (1999) measurements of the effects of air velocity on the magnitude of the mass transfer coefficient. In their experiment, mass transfer coefficient measurements were made to represent conditions in barns with a deep pit manure management system. Therefore the air velocity was varied from 0.1-0.5 ms^{-1}, which using the power law profile represents a wind speed at 10m of ~0.2-1.0 ms^{-1}. Therefore, in this study, air velocity was extrapolated for wind speeds less than 0.2 ms^{-1} and greater than 1 ms^{-1}. Additionally, the exponential negative relationship between air velocity and the mass transfer coefficient is not theoretically supported. As mentioned in section 2.2.7, the overall mass transfer

coefficient is the sum of the resistance in the liquid and gas films. The relative contribution of the liquid and gas films to the total resistance is controlled by the solubility of the chemical compound (Lewis and Whitman, 1924; Liss and Slater, 1974). For highly soluble gases (e.g. ammonia), the resistance is dominated by the gas film (Lewis and Whitman, 1924; Liss and Slater, 1974), whereas for less soluble gases such as H_2S the resistance is controlled by the liquid film (Lewis and Whitman, 1924). Therefore for highly soluble gases like ammonia, an increase in wind speed will decrease the thickness of the gas film, which will decrease the resistance, thus resulting in an increase in the mass transfer coefficient. However for H_2S, a reduction in the thickness of the gas film will have less of an impact in decreasing resistance, resulting in little or no effect on the mass transfer coefficient. It can be concluded that theoretical considerations show that wind speed can have a positive or zero effect in increasing the mass transfer co-efficient. However, there is though no theoretical support for wind speed to decrease the mass transfer coefficient as it increases.

Accordingly, the Arogo et al. (1999) mass transfer coefficient was only used for wind velocities greater than 0.2 ms^{-1} at a height of 10 m, when the effect of wind velocity on the mass transfer coefficient follows more closely the expected theoretical trend.

To further investigate the effect of environmental parameters on predicted flux, the ranges of the environmental parameters from the measurement study were used to calculate the % relative change in predicted flux. The environmental parameter ranges, the predicted fluxes and % relative change values are presented in Table 2.8.

The pH and total sulfide content of manure had the largest % relative changes in predicted flux. As pH increased across the range, predicted flux decreased by ~ 895%. Predicted H_2S flux was found to increase by ~ 542% as sulfide increases across the range. This value was calculated using a minimum sulfide value of 1mg L^{-1}. As discussed, the extent to which sulfide samples were below 1 mg L^{-1} is unknown. However, if the minimum measured sulfide value was 0.63 mg L^{-1} or lower, then sulfide would have greatest % relative change, and thus would be the most influential environmental parameter. These two parameters are significantly more influential than the other environmental parameters. Wind speed was found to decrease predicted H_2S flux by ~37%, using 0.2 ms^{-1} as the minimum of the range. As air temperature increased across the range, predicted H_2S flux decreased by ~ 12%. Lagoon temperature was the environmental parameter which had the least effect on predicted H_2S fluxes. Predicted H_2S fluxes increased by ~7%, when lagoon temperature was varied across it's range.

2.3.3.2. Evaluation of Air-Manure Interface Mass Transfer Model

The A-MI mass transfer model was evaluated by substituting the measured environmental parameters during lagoon sampling into the model. These predicted H_2S flux values were then compared to the corresponding measured H_2S lagoon flux values. It should be noted that predicted H_2S fluxes could only be modeled, when a full set of measured environmental parameters were available. Additionally as mentioned earlier, data where the wind speed was < 0.2 ms^{-1} at a height of 10 m was not included. The relationship between measured and predicted H_2S fluxes were determined using the coefficient of determination (r^2), and is shown in Figure 2.16. It can be observed that the

model performs fairly well in predicting H_2S fluxes with an r^2 value of 0.57 ($p<0.0001$). The mean response for this relationship is 1.090 with a 95% confidence interval of ± 0.796. Further evaluation of the performance of the model was conducted by calculating the mean bias (Equation 24), the normalized mean bias (Equation 25), the mean error (Equation 26) and the normalized mean error (Equation 27).

$$\frac{1}{N}\sum_{i=1}^{N}(J_{\mathrm{mod}}(i)-J_{meas}(i)) \tag{24}$$

$$\frac{1}{N}\frac{\sum_{i=1}^{N}J_{\mathrm{mod}}(i)-J_{meas}(i)}{\sum_{i=1}^{N}J_{meas}(i)}\times 100\% \tag{25}$$

$$\frac{1}{N}\sum_{i=1}^{N}\left|J_{\mathrm{mod}}(i)-J_{meas}(i)\right| \tag{26}$$

$$\frac{1}{N}\frac{\sum_{i=1}^{N}\left|J_{\mathrm{mod}}(i)-J_{meas}(i)\right|}{\sum_{i=1}^{N}\left|J_{meas}(i)\right|}\times 100\% \tag{27}$$

where N is the number of data points, J_{mod} and J_{meas} are the corresponding model predicted and measured flux values and *i* the *i*th model-measurements data points. The model was found to slightly over predict measured fluxes with a mean bias value of 0.121 μg m^{-2} min^{-1}, and a normalized mean bias value of 0.008%. The mean error and normalized mean error values were 0.641 μg m^{-2} min^{-1} and 0.040%, respectively.

The accuracy of the A-MI mass transfer model in predicting H_2S emissions can be rationalized by comparing it to the statistical observational model developed based on the measurement data. Both models show pH to have a large effect on H_2S emissions and that increasing pH, decreases emissions. Also both models agree that lagoon temperature

has a smaller effect on emissions, and that as temperature increases, emissions increase. However, a difference in the models can be observed for air temperature. In the A-MI mass transfer model, emissions have a slight decreasing trend, as air temperature increases. However, the statistical observation model shows a slight increase in fluxes as air temperature increases.

A further difference between the A-MI model and the statistical observational model is related to the effect of wind speed. The statistical model does not include the effect of wind speed, since the chamber air-lagoon interface wind speed may be different from ambient conditions. However, the A-MI mass transfer model shows a slight decrease in fluxes as wind speed increases. As mentioned, sulfide content could not be statistically analyzed due to low sulfide concentrations, therefore the effect of this environmental parameter cannot be compared.

From this analysis, it can be concluded that the A-MI mass transfer model does well in modeling the effect of pH and lagoon temperature. There is though a disagreement on the effects of air temperature. However, this is not thought to be of concern as the A-MI mass transfer model only models a slight decrease.

The accuracy of the model was further determined by comparing measured average seasonal fluxes with predicted average seasonal flux using the corresponding average seasonal environmental parameters values, as shown in Table 2.9. The A-MI mass transfer model was accurate in predicting flux. For both the fall and spring season, the model performed very well. In the fall, predicted flux exactly matched the measured flux (1.17 $\mu g\ m^{-2}\ min^{-1}$). For spring, the predicted flux was only 0.01 $\mu g\ m^{-2}\ min^{-1}$ less

than the measured flux value, 0.26 μg m^{-2} min^{-1} compared to 0.27 μg m^{-2} min^{-1}, respectively. The flux was slightly under predicted in the summer with a predicted flux of 3.05 μg m^{-2} min^{-1}, and a measured flux of 3.81 μg m^{-2} min^{-1}. Conversely, the flux was slightly over predicted in the winter, with a predicted flux value of 0.34 μg m^{-2} min^{-1} compared to a measured flux of 0.08 μg m^{-2} min^{-1}. It should be noted that the sulfide levels used for this comparison are maximum possible concentrations, assuming that each sample that was below the detection limit of 1 mg L^{-1} was equal to 1 mg L^{-1}.

2.3.3.3. Application of Process Based Air-Manure Interface Mass Transfer Model to Predict CAFO Emissions from Manure Surfaces

The process based air-manure interface mass transfer model developed in this study performed well in predicting H_2S emissions from an anaerobic lagoon at a swine CAFO. However, it is hypothesized that this model may be used to predict H_2S emissions from a variety of CAFO manure surfaces, thus allowing a method for quantifying emissions in different production, management and environmental conditions. This is due to the different approaches used to develop the main components of the model, which can take into account differences in manure characteristics.

The dissociation constant can be applied to other manure surfaces, as the calculation of the activity coefficient used to correct the dissociation constant only requires the measurement of manure electrical conductivity. The Henry's law constant used in this study can be assumed to be the same for all manures. As discussed, previous experimental studies have found no significant difference in the Henry's law constant between water and municipal wastewater (Al-Haddad et al. 1989; Yongsiri et al. 2005).

The mass transfer coefficient used in this study could also be applied to predict emissions from a variety of manure surfaces, however there are two issues to consider, the representation of the effect of air velocity on the mass transfer coefficient as determined by Arogo et al. (1999), and the effect of manure solid content on the mass transfer coefficient. The effect of air velocity on the mass transfer coefficient when taking into account theoretical considerations, does not seem to be an accurate representation. The effect of manure solid content on the mass transfer coefficient is unknown. Arogo et al. (1999) reported that between water and <1% solid manure, there was a statistically significant difference in the mass transfer coefficient with respect to air velocity. However, it is not known if this effect continues with increasing manure solid content.

Additionally, it is hypothesized that this process based model could be applied to other trace gas CAFO emissions. Both the dissociation constant and the Henry's law constant are based on thermodynamic principles, which can be applied to a range of chemical compounds. The only requirement for the model is information on the behavior of the compounds' mass transfer coefficient at the air-manure interface in different environmental conditions.

2.4. CONCLUSIONS

Measurements of H_2S emissions from an anaerobic lagoon and barn were made over four seasonal sampling periods at a swine CAFO in North Carolina. The H_2S emissions were evaluated with respect to diurnal and seasonal variations and environmental parameters. Additionally, a process based air-manure interface mass

transfer model was developed to predict H_2S manure emissions. Different approaches based on thermodynamic principles and related published information were used to determine the three main components of the model: the overall mass transport coefficient, the dissociation constant, and the Henry's law constant. The accuracy of this model was evaluated by comparing predicted H_2S fluxes to measured H_2S lagoon fluxes.

Seasonal measured H_2S lagoon fluxes were found to range from 0.08 ± 0.09 μg m^{-2} min^{-1} in the winter to 3.82 ± 3.24 μg m^{-2} min^{-1} in the summer. The effect of environmental parameters on measured H_2S lagoon fluxes were determined by statistical analysis. pH was found to have the largest influence on flux, followed by lagoon temperature and wind speed. Average seasonal barn concentrations were found to range from 72 ± 43 ppb in the summer to 631 ± 240 ppb in the spring. Barn emissions were also highest in the spring with a value of 7.31 ± 2.48 g day^{-1} AU^{-1}. The lowest barn emissions were in the winter with an emission of 0.81 ± 0.48 g day^{-1} AU^{-1}. Due to the nature of the barn environment, it is hard to determine the influence of environmental parameters. However, barn temperature was found to have a weak correlation with H_2S emissions ($r^2 = 0.19$, $p<0.0001$).

The process based air-manure interface mass transfer model did well in predicting H_2S fluxes, when compared with 15 minute average lagoon fluxes ($r^2 = 0.57$, $p<0.0001$). The model also performed well in predicting seasonal lagoon fluxes. It is hypothesized that with good estimations of the overall mass transport coefficient, that this model could be applied to predict trace gas CAFO emissions from a variety of manure surfaces, thus

providing a method for quantifying emissions in different production, management and environmental conditions.

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Table 2.1. Lagoon H_2S fluxes and corresponding environmental parameters

Season/ Sampling date	Flux ($\mu g\ m^{-2}\ min^{-1}$)	Lagoon Temperature (^oC)	Lagoon pH	Air temperature (^oC)	Wind Speed (m/s)	Sulfide ($mg\ L^{-1}$)
Summer	3.81[a]	25.89	7.26	21.91	1.38	1.83[d]
	(3.24)[b]	(2.74)	(0.12)	(4.90)	(1.05)	(1.68)
	N = 705[c]	N = 676	N=520	N = 705	N = 705	n = 12 (8)[e]
Fall	1.17	20.54	7.52	17.81	1.68	1.48
	(1.62)	(2.91)	(0.10)	(6.43)	(1.69)	(1.09)
	N = 646	N= 645	N = 559	N= 646	N=646	n= 12 (9)
Winter	0.08	12.23	8.02	6.97	2.05	1.56
	(0.09)	(2.14)	(0.14)	(5.73)	(1.19)	(1.04)
	N = 631	N= 605	N = 631	N= 631	N = 631	n= 12 (6)
Spring	0.27	19.93	8.03	14.45	2.76	1.19
	(1.71)	(2.09)	(0.10)	(6.81)	(1.74)	(0.28)
	N = 478	N = 478	N = 469	N= 469	N = 469	n = 10 (7)

[a] Mean value

[b] ±1 Standard Deviation

[c] N represents the number of 15 minute averaged data points

[d] The maximum possible average of sulfide concentration, assuming that the sulfide samples below the detection limit are equal to 1 $mg\ L^{-1}$

[e] number of anaerobic lagoon samples collected, number in parentheses represent the number of samples at detection limit of 1 $mg\ L^{-1}$

Table 2.2. H_2S fluxes from previous swine CAFOs lagoon studies.

Reference	Location	Sampling Period	Lagoon Temperature (^oC)	pH	Sulfide Concentration ($mg\ L^{-1}$)	H_2S flux ($\mu g\ m^{-2}\ min^{-1}$)
Zahn et al. (2001)	MO	August	-	8.1	15	438
Zahn et al. (2001)	MO	September	-	8.2	17	492
Zahn et al. (2001)	MO	October	-	8.1	18	1266
Lim et al. (2003)	Midwest[a]	April-July	25	8.1	-	546
Lim et al. (2003)	Midwest[a]	April-July	25	7.9	-	138
Byler et al. (2004)	NE	May-June	-	7.8	-	114
Byler et al. (2004)	NE	May-June	-	7.4	-	192
Byler et al. (2004)	NE	July-August	-	8.1	-	4.2
Byler et al. (2008)	NE	July-August	-	7.7	-	19.2
Blunden and Aneja (2008)	NC	October-November	18	8.1	0.6	0.3
Blunden and Aneja (2008)	NC	February	12	8.1	3.2	~0.0
Blunden and Aneja (2008)	NC	April	15	8.1	1.8	0.5
Blunden and Aneja (2008)	NC	June	30	8.0	9.2	5.3
This study	NC	June	26	7.3	1.8[b]	3.8
This study	NC	October-November	21	7.5	1.5[b]	1.2
This study	NC	February	12	8.0	1.6[b]	0.1
This study	NC	April	20	8.0	1.2[b]	0.3

[a] Location is assumed to be the Midwest of the U.S., location is not specified in paper

[b] Maximum possible average of sulfide concentration, assuming that the sulfide samples below the detection limit are equal to 1 $mg\ L^{-1}$.

Table 2.3. pH values from swine CAFO lagoons in North Carolina

Reference	Sampling Period	Lagoon pH	Description of Sampling Methodology
Blunden et al. (2008)	Fall	8.1[a] (~ 0.0)[b], 8.0-8.2[c]	one lagoon
	Winter	8.1 (~ 0.0), 8.0-8.2	continuously measured
	Spring	8.1 (~ 0.0), 8.0-8.2	for a ~1 week period
	Summer	8.0 (0.1), 7.9-8.1	
Aneja et al. (2000)	Summer	7.5 (0.18), 7.1-7.8	one lagoon
	Fall	8.0 (0.06), 7.9-8.1	continuously measured
	Winter	7.8 (0.13), 7.66-8.02	for a 1-2 week period
	Spring	7.7 (0.06), 7.64-7.81	
Bicudo et al. (1999)	-	7.6-8.0[d] (0.1)[e]	15 lagoons measured ~once/month for 2 years
Biological & Agricultural Engineering (1994)	-	7.8[f] (0.24), 7.0-8.5	179 samples taken from a range of lagoons
This study	Summer	7.26 (0.12), 7.10-7.69	one lagoon
This study	Fall	7.52 (0.10), 7.31-7.82	continuously measured
This study	Winter	8.02 (0.14), 7.27-8.25	for a ~1 week period
This study	Spring	8.03 (0.10), 7.71-8.32	

[a] Mean value
[b] ± 1 standard deviation
[c] Range
[d] Range of averages from 15 lagoons
[e] Average standard deviation from 15 lagoons
[f] All values are based on 179 observations, the number of different lagoons is not known

Table 2.4. r^2 values and corresponding p-values for the relationship between H_2S flux and environmental parameters.

	pH	Lagoon Temperature	Air Temperature
r^2	0.74	0.44	0.33
p-value	<0.0001	<0.0001	<0.0001

Table 2.5. Seasonal statistics for the barn measurements.

	H_2S Emissions (g day^{-1})	H_2S Concentration (ppb)	Ventilation rate (m^3 min^{-1})	Barn temperature (^oC)	Ambient temperature (^oC)
Summer	189[a]	72	1763	27.9	26.0
	(42)[b] N[c] =518	(43), 73[d]	(691)	(2.7)	(4.1)
Fall	206	327	327	19.9	8.4
	(88) N=741	(158), 307	(180)	(2.4) N =740	(5.2)
Winter	79	165	269	18.4	11.3
	(54) N =507	(64), 150	(181)	(3.8)	(6.2)
Spring	647[e]	631[e]	626	26.5	19.0
	(219) N =649	(240), 645	(350)	(1.5) N =630	(4.2) N =632

[a] Mean value
[b] ±1 standard deviation
[c] N represents the number of 15 minute averaged data points collected in each sampling season for H_2S concentration, ventilation rate and all corresponding environmental parameters, unless stated.
[d] Average daily mean value
[e] 27% of the 15 minute averaged data points, had at least one minute average concentration above the limit of detection of the analyzer (1000 ppb).

Table 2.6. Seasonal pig production information and the calculated normalized H_2S emission rate.

Sampling Season	Number of Pigs	Number of weeks in rotation	Average Weight (kg)	Total Live Animal Weight (kg)	Normalized H_2S emission rate (g day^{-1} AU^{-1})
Summer	884.5	7-8	48.7	43,049	2.20 (0.49)[a]
Fall	994.5	4-5	34.6	34,428	2.99 (1.27)
Winter	476[b]	20-21	116.6	55,513	0.71 (0.48)
Spring	874.5	8-9	50.6	44,262	7.31 (2.48)

[a] ±1 standard deviation

[b] Occurred at end of rotation, when some pigs had been sold.

Table 2.7. Previous studies H_2S concentrations and emissions.

Reference	Location of study	Ventil-ation type	Manure collection system	Month	ADM[e] Conce-ntrat-ion (ppb)	Total live animal weight (kg)	Emission rate (H_2S g day^{-1} AU)
Heber et al. (1997)	Midwest[a]	NV	Deep pit	Jan-Mar	180	-	0.84
Ni et al. (2002)	IL	MV	Deep pit	Jun-Sep	173	48,783	8.3
Zhu et al. (2000)	Midwest[a]	MV	Deep pit	Sep	414	44,990	2.0[c]
Zhu et al. (2000)	Midwest	NV	Deep pit	Sep	271	43,640	3.32
Jacobson et al. (2003)	MN	NV	Deep bedded	Dec	10.1[b]	-	0.11[d]
Jacobson et al. (2003)	MN	NV	Deep bedded	Jun-Jul	8.7	-	0.16
Heber et al. (2004)	Midwest[a]	MV	Shallow pit/Flush daily	Aug-Nov	141[b]	79,650	1.34
Heber et al. (2004)	Midwest	MV	Shallow pit/Flush daily	Dec-Mar	73.5	74,324	0.35
Heber et al. (2004)	Midwest	MV	Shallow pit/Flush daily	May-Aug	171	94,329	0.80
Kim et al. (2008)	S. Korea	NV	Deep pit	May-Jun & Sep-Oct	296.3[b]	-	6.7[c]
Kim et al. (2008)	S. Korea	MV	Deep pit	May-Jun & Sep-Oct	612.8	-	8.5
Kim et al. (2008)	S. Korea	NV	Scraper removal	May-Jun & Sep-Oct	115.2	-	5.8
Kim et al. (2008)	S. Korea	MV	Scraper removal	May-Jun & Sep-Oct	270.3	-	6.3
Kim et al. (2008)	S. Korea	NV	Deep bedded	May-Jun & Sep-Oct	137.8	-	3.0
Blunden et al. (2008)	NC	MV	Shallow pit/Flush weekly	Feb	632	48,963	4.2
Blunden et al. (2008)	NC	MV	Shallow pit/Flush weekly	Apr	441	73,895	3.3
Blunden et al. (2008)	NC	MV	Shallow pit/Flush weekly	Jun	47	33,952	1.2
Blunden et al. (2008)	NC	MV	Shallow pit/Flush weekly	Oct	304	38,390	1.7
This study	NC	MV	Shallow pit/Flush weekly	Jun	73	43,049	2.20
This study	NC	MV	Shallow pit/Flush weekly	Nov	307	34,428	2.99
This study	NC	MV	Shallow pit/Flush weekly	Feb	150	55,513	0.81
This study	NC	MV	Shallow pit/Flush weekly	Apr	645	44,262	7.31

[a] Location is assumed to be Midwest of U.S, location is not specified in paper
[b] Concentrations presented from this study are average concentrations, instead of average daily mean concentrations
[c] Emissions calculated for this study are based on data presented in the paper
[d] Emission numbers for this study are based on comment in Jacobson et al. (2004)
[e] ADM = Average daily mean

Table 2.8. % relative change in predicted fluxes as environmental parameters vary across the measurement range.

Parameter	Range	Predicted flux from minimum of range	Predicted flux from maximum of range	% relative change
Sulfide	1-6.4	1.39	8.92	542
pH	7.10-8.32	3.78	0.38	895
Lagoon Temperature	8.85-34.13	0.70	0.74	6
Air Temperature	-4.28-34.92	0.70	0.80	12.5
WS	0.2-7.55	0.97	0.61	37

Table 2.9. Average measured and model predicted H_2S seasonal flux values.

Season	Sulfide (mg L^{-1})	pH	Lagoon Temper-ature (^oC)	Wind Speed (m s^{-1})	Air Temper-ature (^oC)	Measured flux (μg m^{-2} min^{-1})	Predicted flux (μg m^{-2} min^{-1})
Summer	1.83	7.26	25.89	1.38	21.91	3.81	3.05
Fall	1.48	7.52	20.54	1.68	17.81	1.17	1.17
Winter	1.56	8.02	12.23	2.05	6.97	0.08	0.34
Spring	1.19	8.03	19.93	2.76	14.45	0.27	0.26

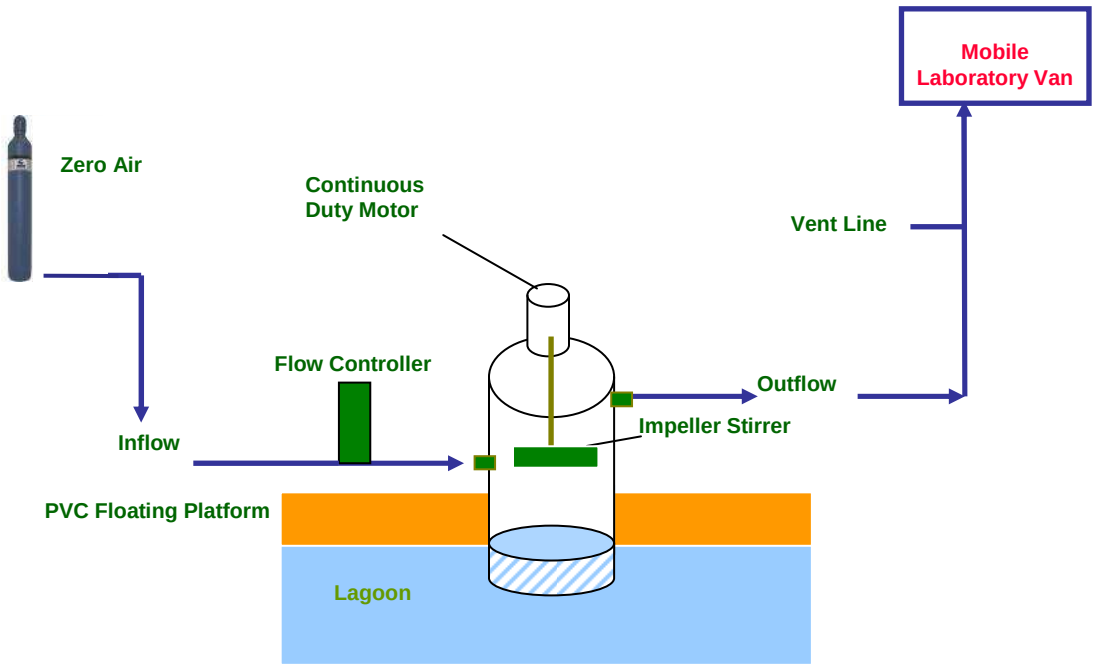


Figure 2.1. Schematic of the dynamic flow-through chamber system.

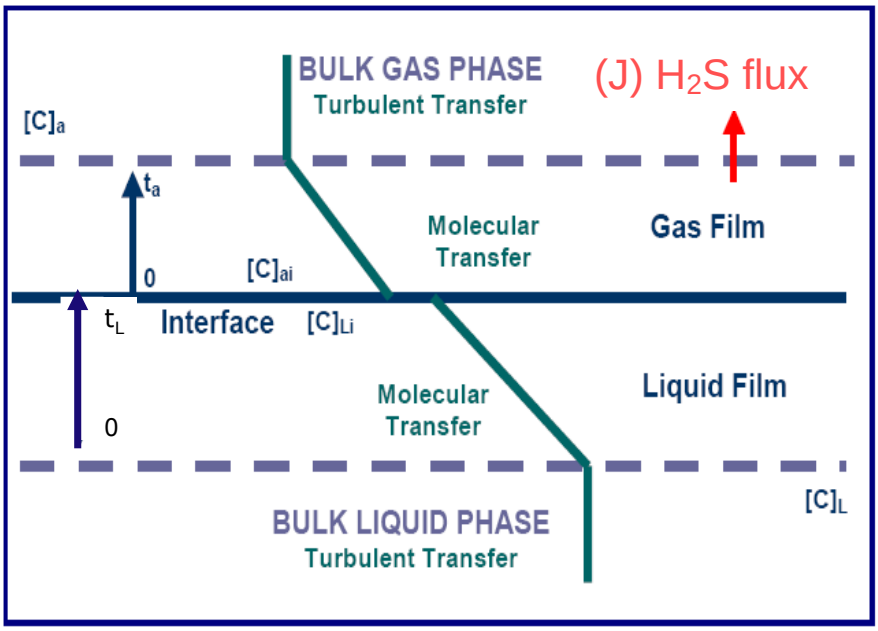


Figure 2.2. Diagram of the two-film mass transfer model.

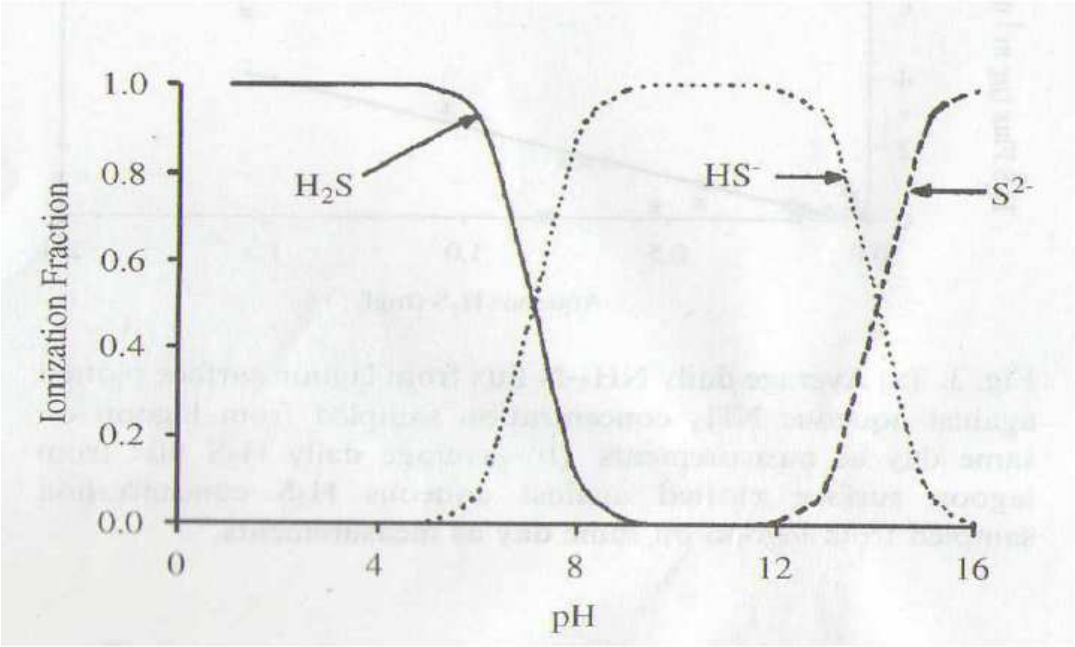
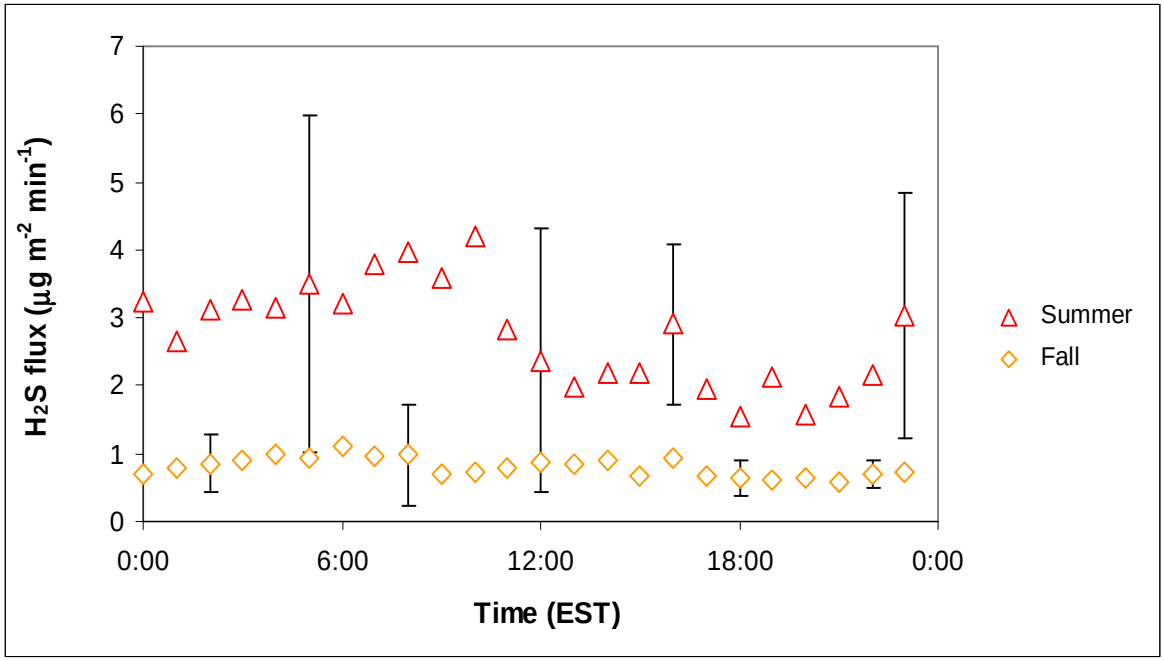


Figure 2.3. The relationship between the fraction of sulfide species (H_2S, HS, S^{2-}) present in aqueous solution and pH at 25^{o}C (from: Snoeyink and Jenkins, 1980).

a)



b)

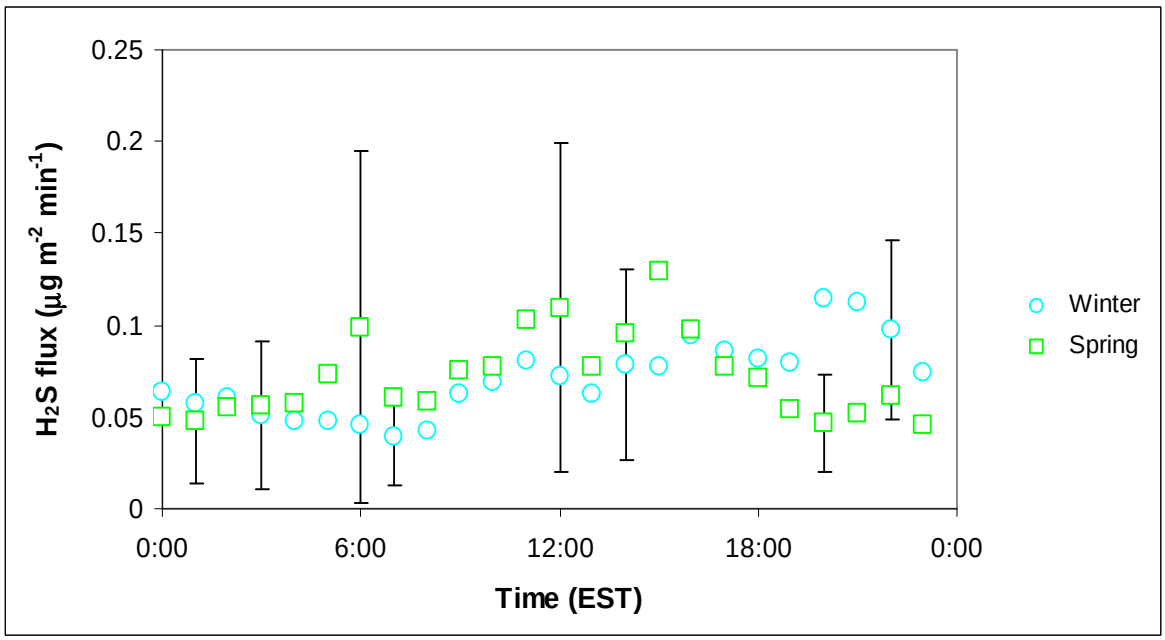


Figure 2.4. The composite hourly average diurnal trend of H_2S flux (µg m^{-2} min^{-1}) for a) the summer and fall sampling season, b) the winter and spring sampling season. Error bars represent ±1 standard deviation and are randomly selected.

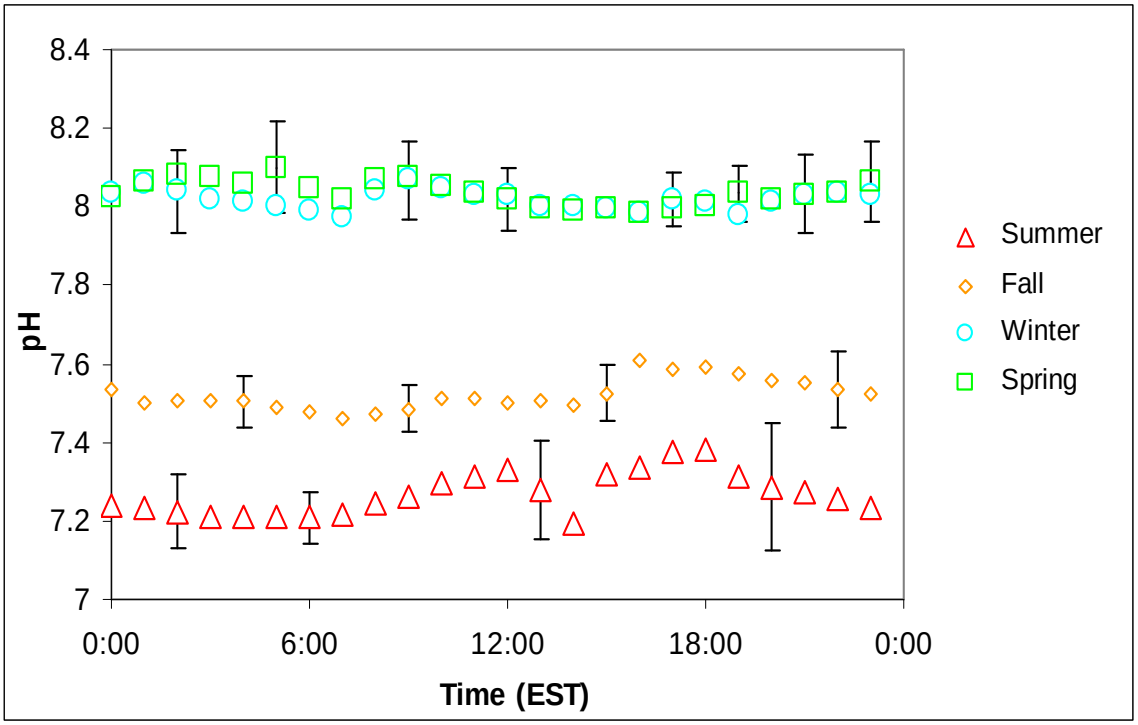
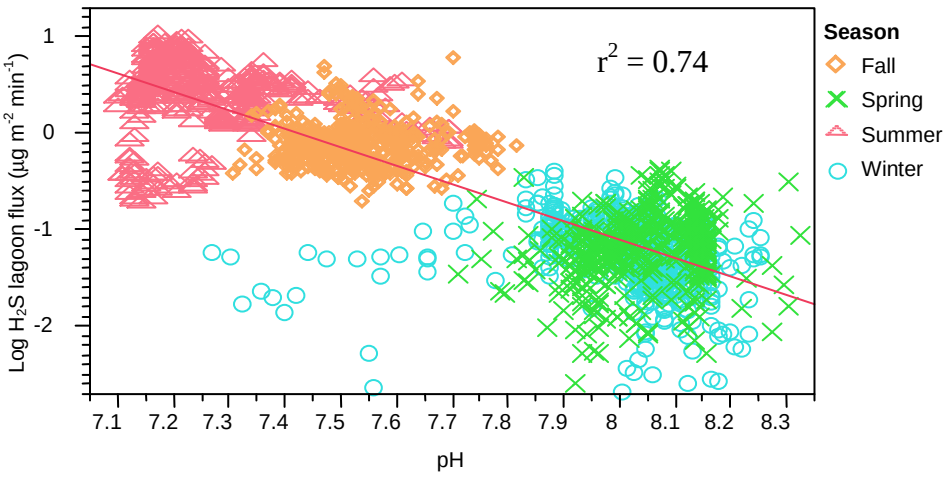


Figure 2.5. The composite hourly average diurnal trend of H_2S flux for the four sampling seasons. Error bars represent ±1 standard deviation and are randomly selected.

a)



b)

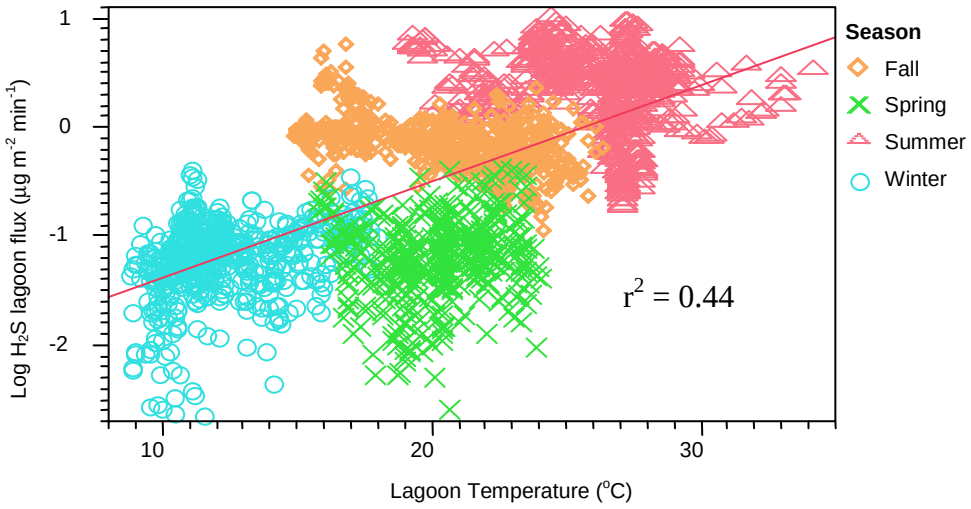


Figure 2.6. Log H_2S lagoon flux vs. a) ph, and b) lagoon temperature.

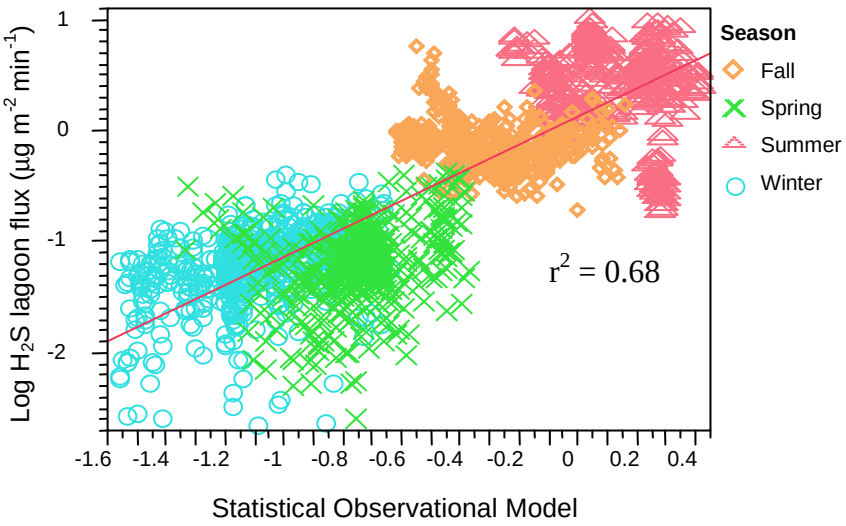
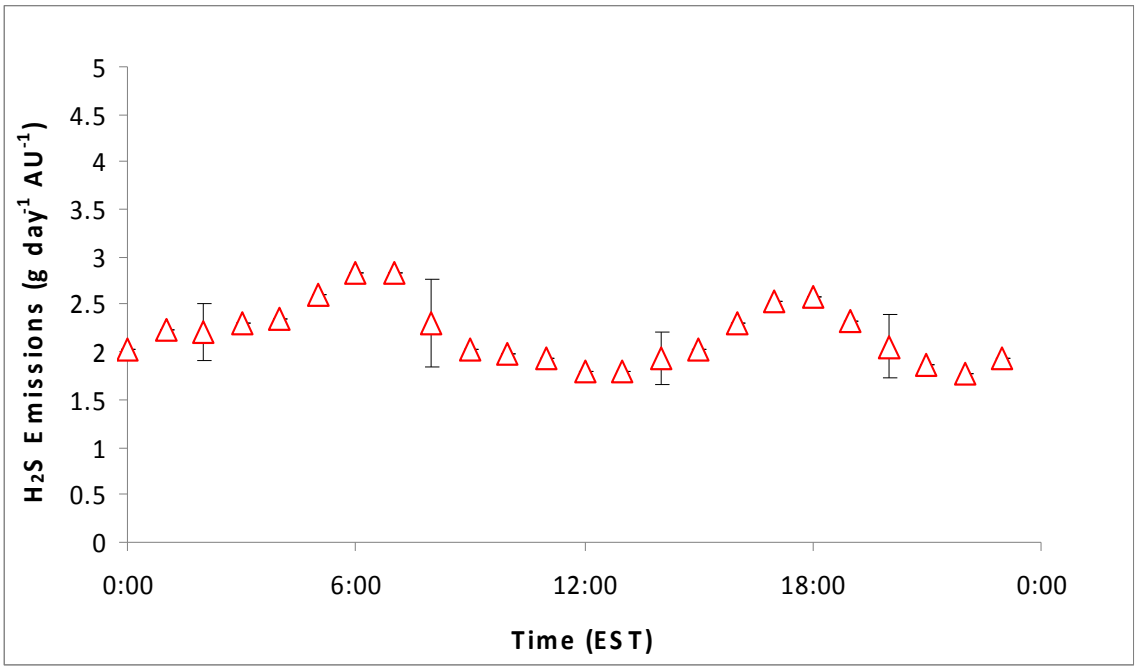


Figure 2.7. The statistical observational model (equation 23) vs. log lagoon H_2S flux (µg m^{-2} min^{-1}). Data points (n= 1806) represent 15 minute averages.

a)



b)

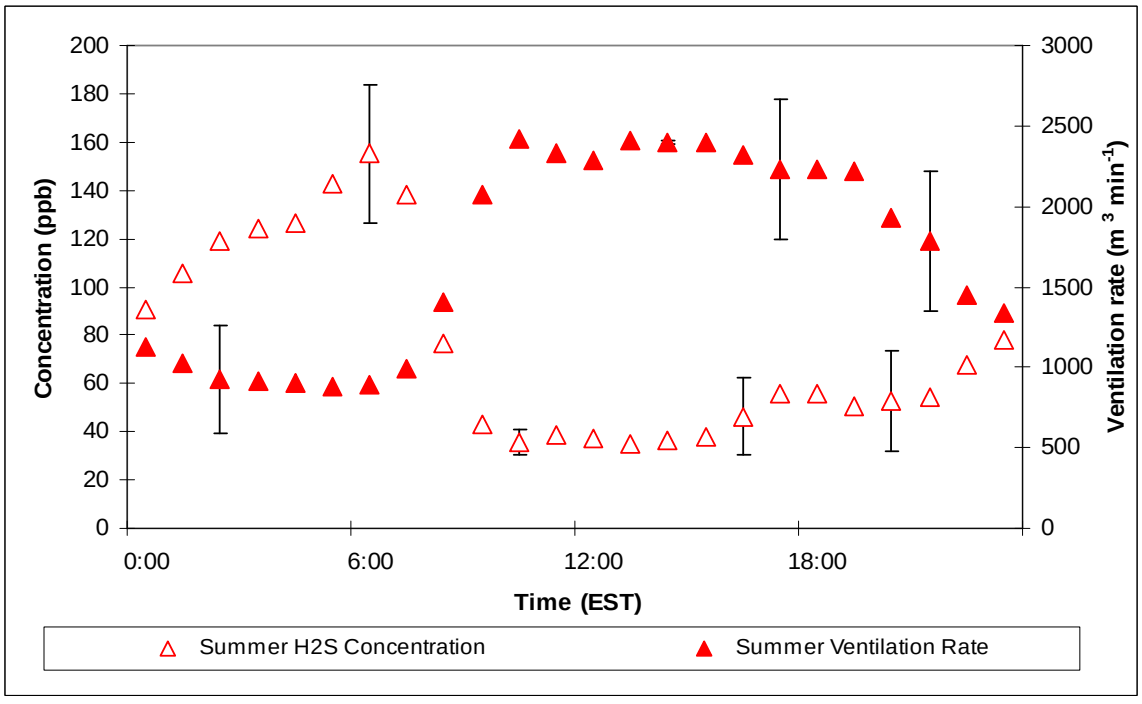
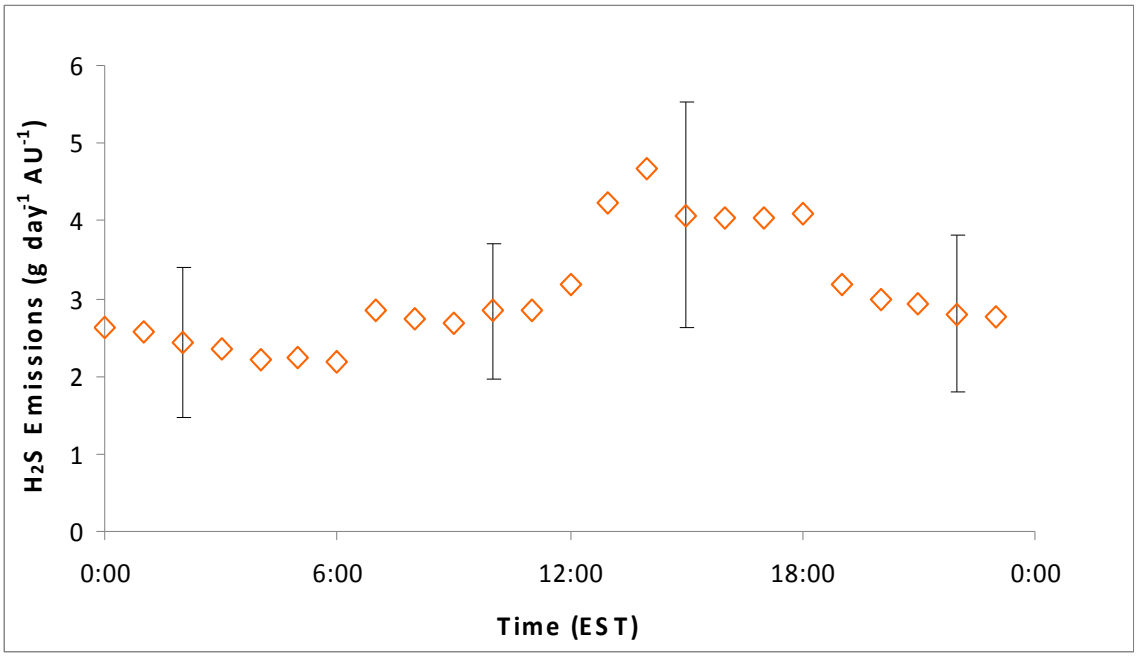


Figure 2.8. Summer composite hourly averaged diurnal trend for a) normalized H_2S emissions and b) H_2S concentration and ventilation rate. Error bars represent ±1 standard deviation and are randomly selected.

a)



b)

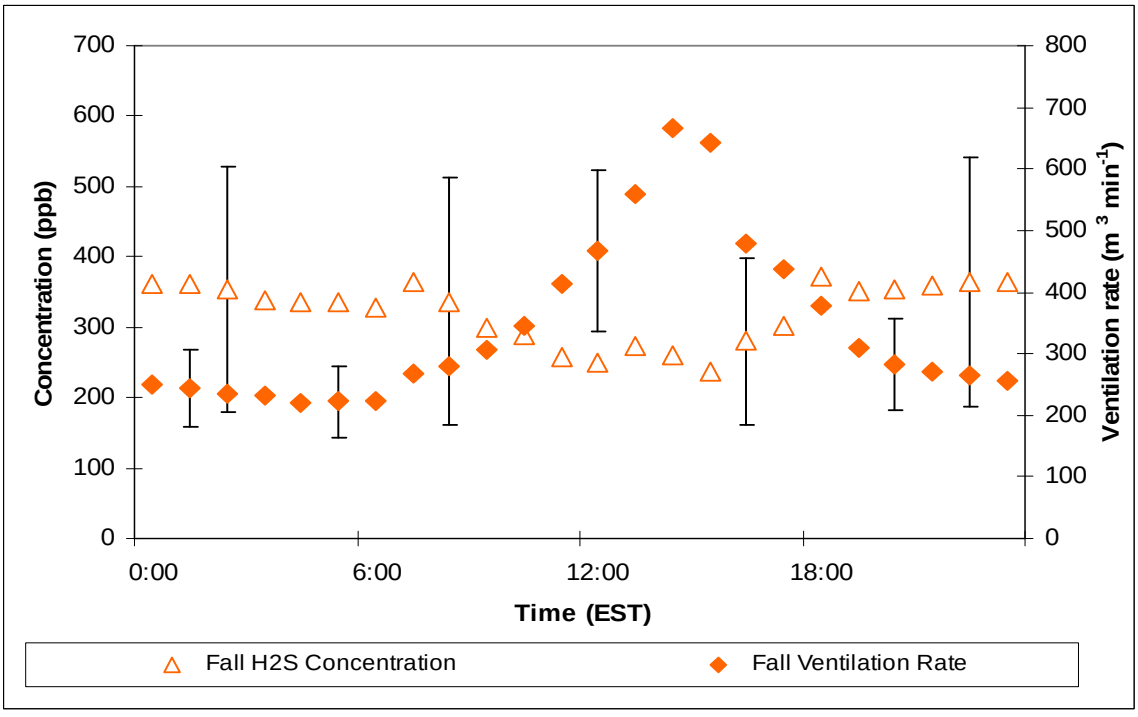
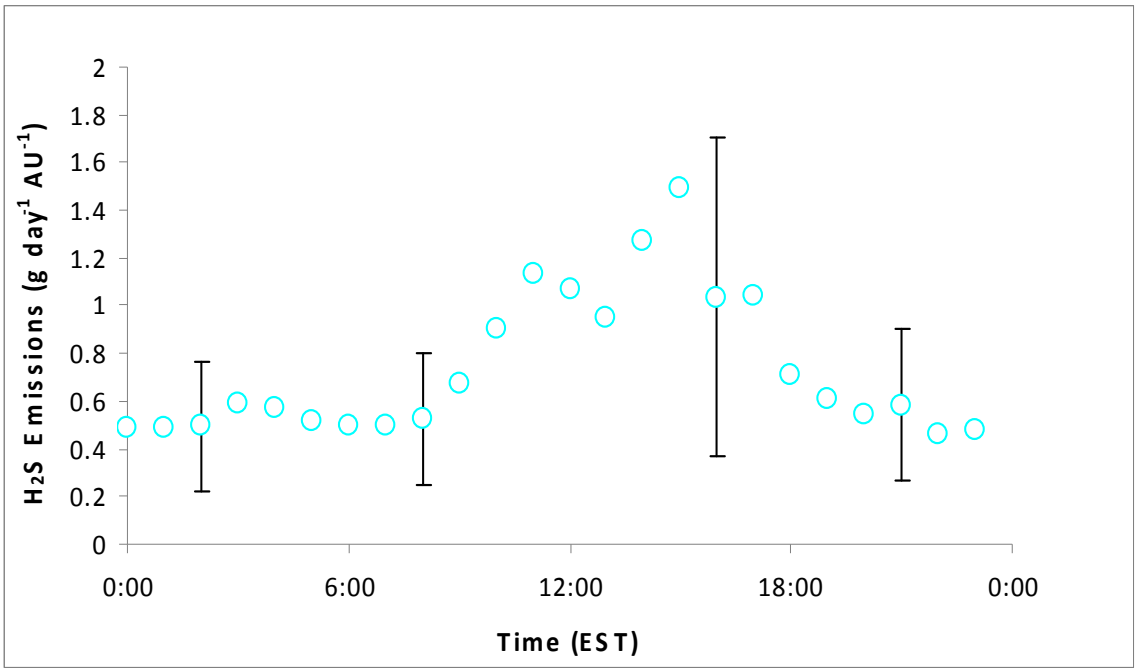


Figure 2.9. Fall composite hourly averaged diurnal trend for a) normalized H_2S emissions and b) H_2S concentration and ventilation rate. Error bars represent ±1 standard deviation and are randomly selected.

a)



b)

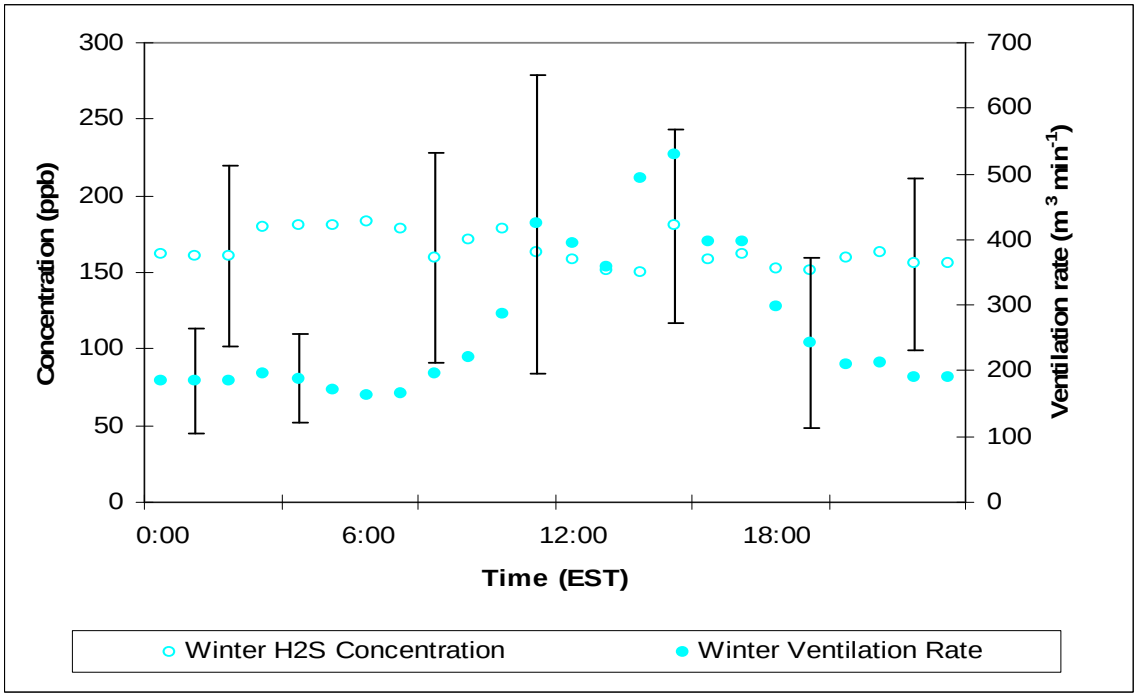
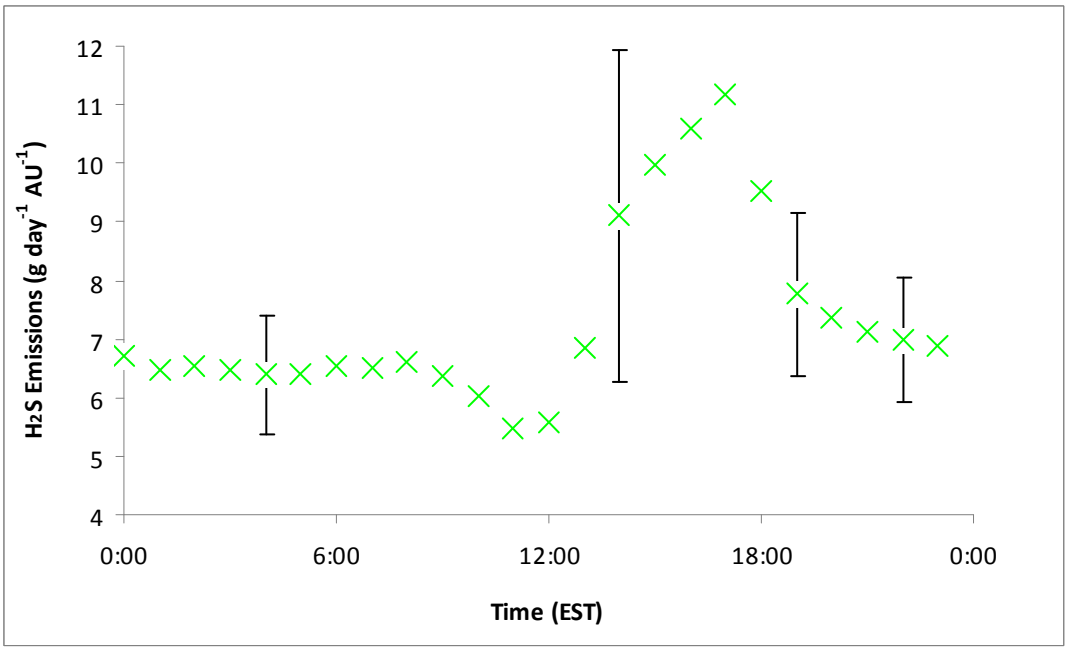


Figure 2.10. Winter composite hourly averaged diurnal trend for a) normalized H_2S emissions and b) H_2S concentration and ventilation rate. Error bars represent ±1 standard deviation and are randomly selected.

a)



b)

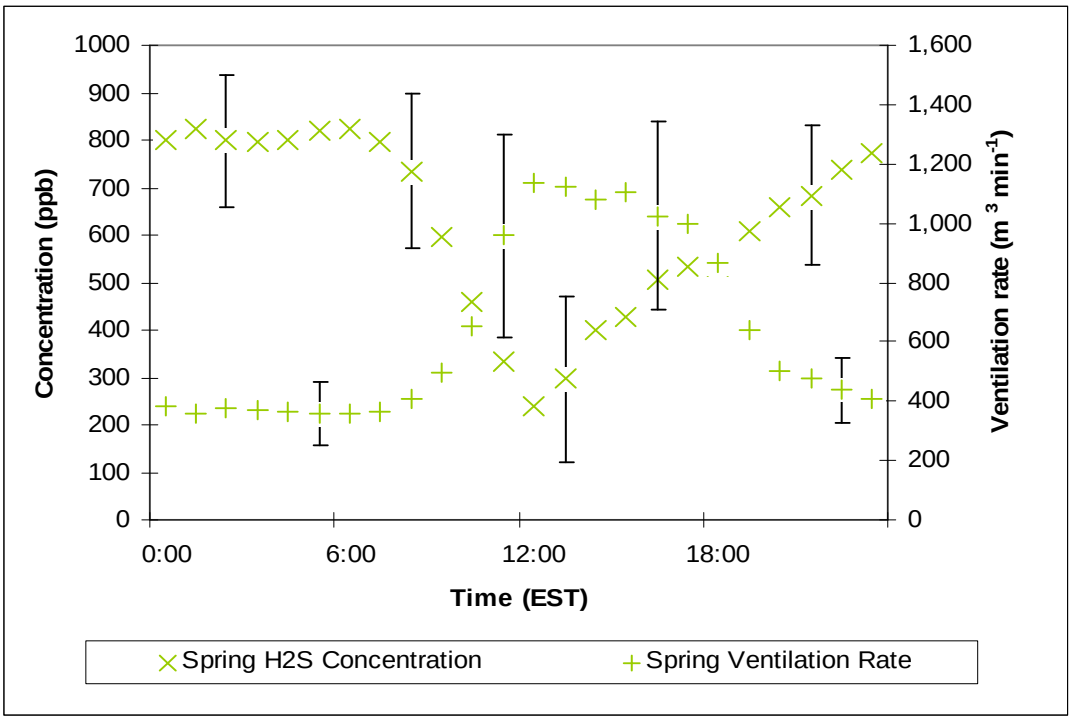


Figure 2.11. Spring composite hourly averaged diurnal trend for a) normalized H_2S emissions and b) H_2S concentration and ventilation rate. Error bars represent ±1 standard deviation and are randomly selected.

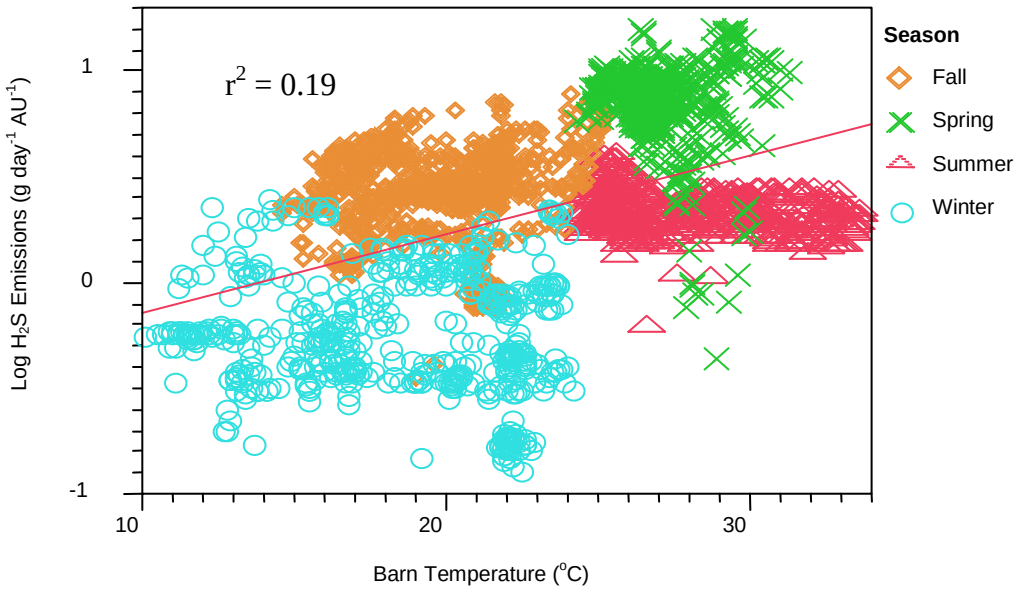
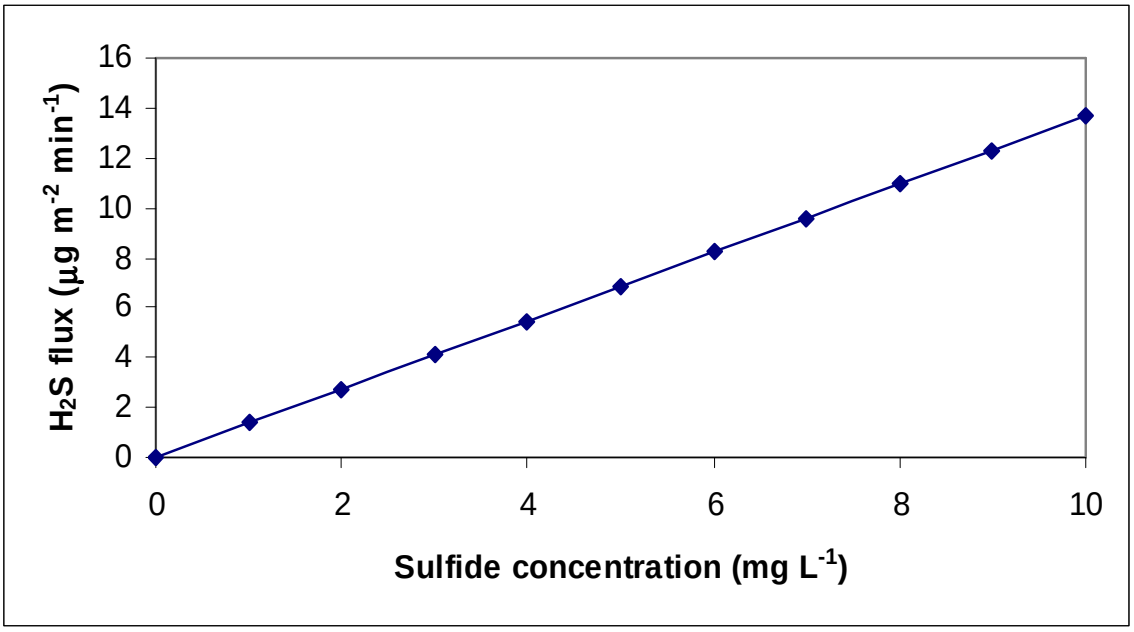


Figure 2.12. The relationship between log H_2S emissions (g day^{-1} AU^{-1}) and barn temperature (^oC). Data points (n=2222) represent 15 minute averages.

a)



b)

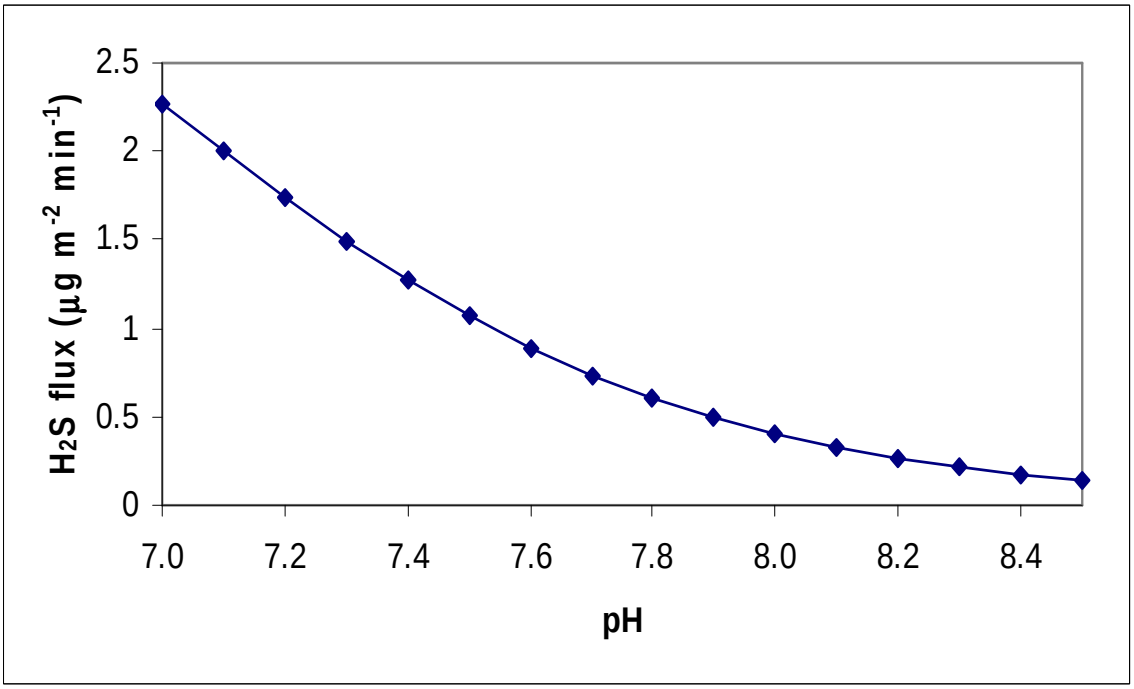
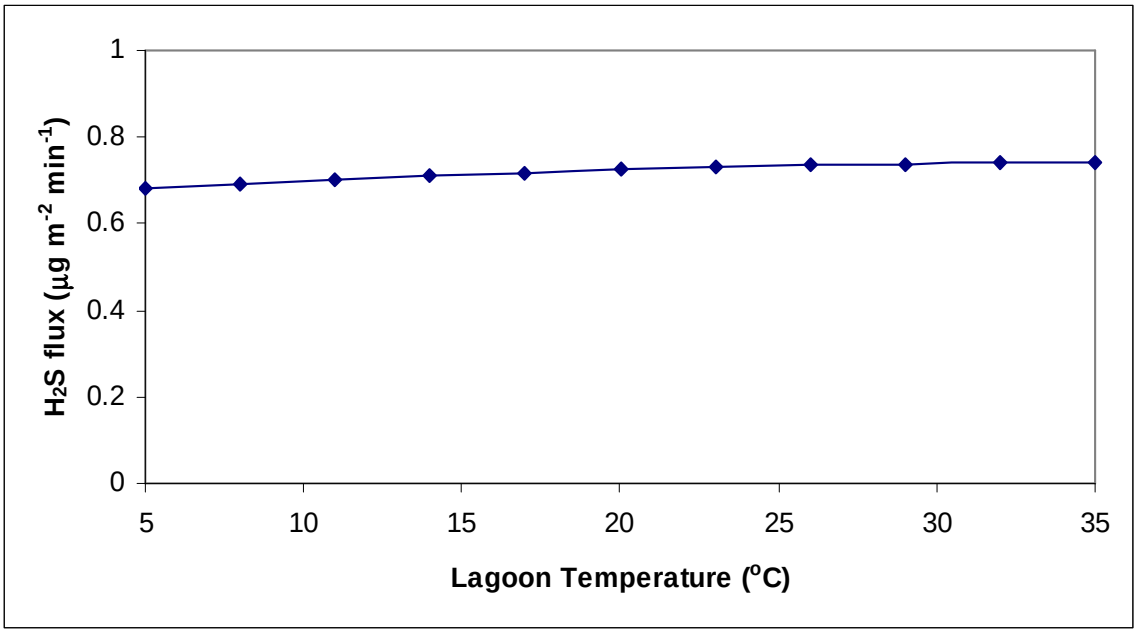


Figure 2.13. Sensitivity analysis of H_2S flux with respect to a) sulfide concentration, and b) lagoon pH.

a)



b)

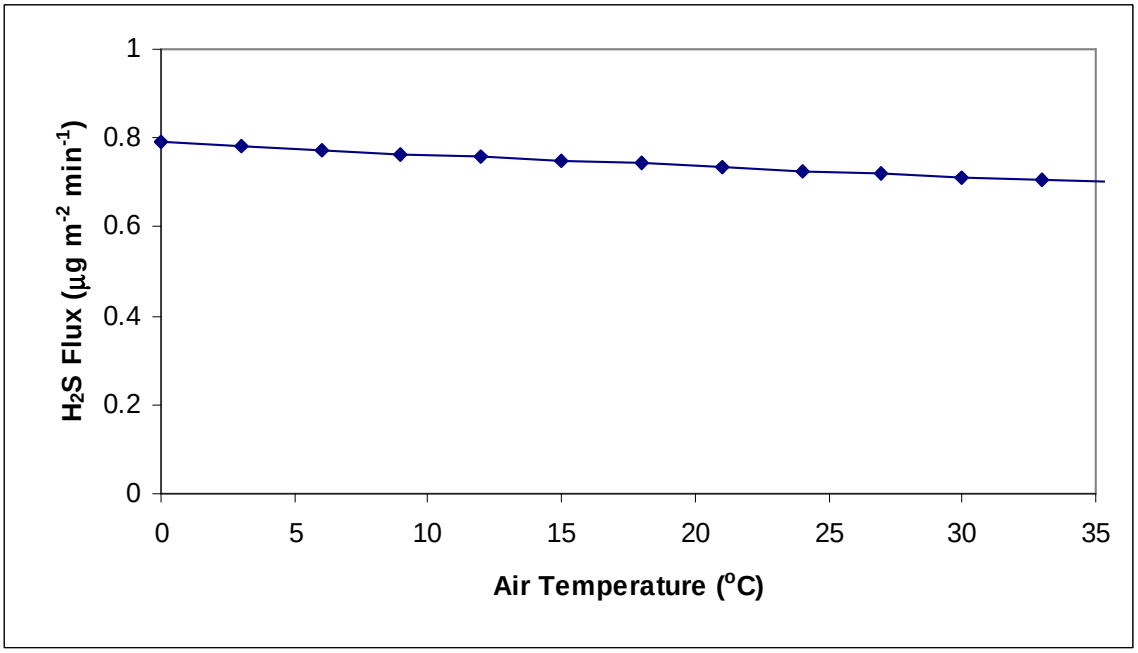


Figure 2.14. Sensitivity analysis of H_2S flux with respect to a) lagoon temperature, and b) air temperature.

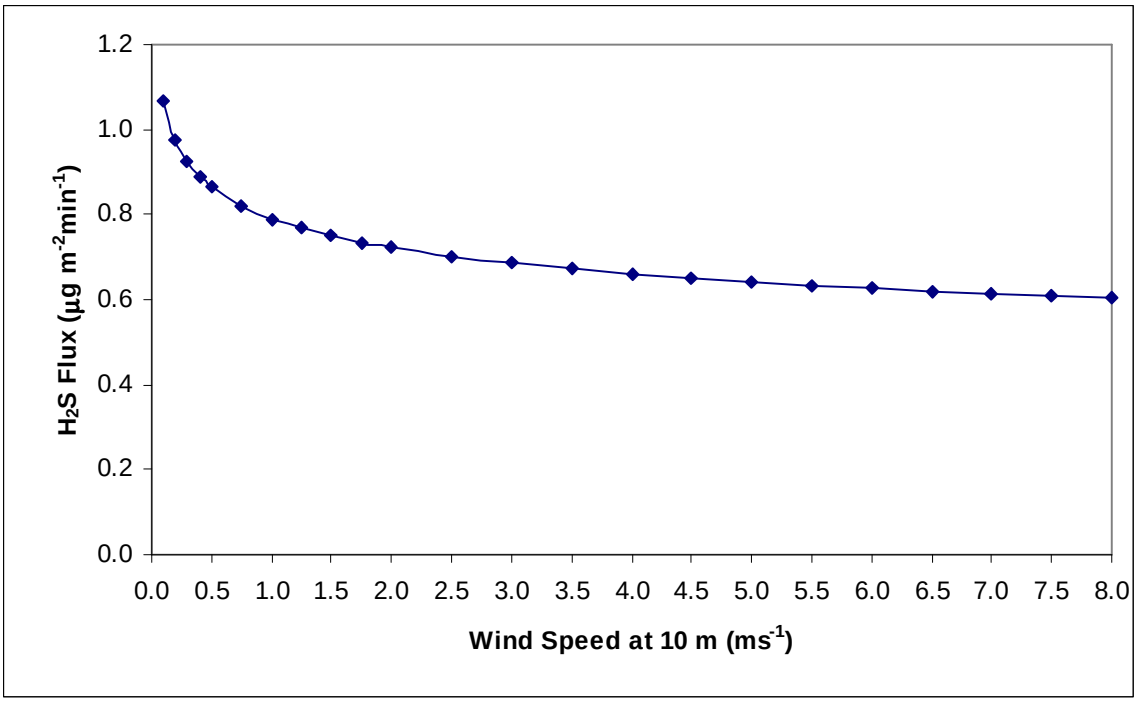


Figure 2.15. Sensitivity analysis of H_2S flux with respect to wind speed.

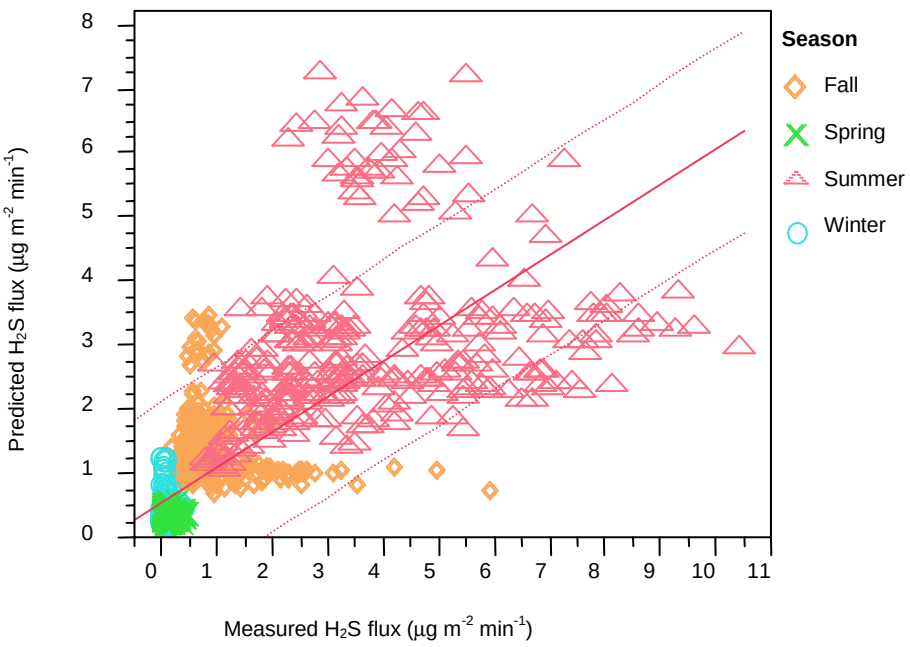


Figure 2.16. Predicted H_2S flux from the H_2S manure emission model vs. corresponding measured flux. Data points (n= 1642) represent 15 minute averages. Dashed red line represents the 95% confidence interval.

Chapter III.
Characterizing Reduced Sulfur Compound Emissions from a Swine Concentrated Animal Feeding Operation

ABSTRACT

Reduced sulfur compounds (RSCs) emissions from concentrated animal feeding operations (CAFOs) have become a potential environmental and human health concern, as a result of changes in livestock production methods. RSC emissions were measured using fused-silica lined (FSL) and SUMMA polished stainless steel canisters and were analyzed ex-situ using a gas chromatography system with a flame ionization detector (GC-FID). Nine to eleven canister samples were taken each from both an anaerobic lagoon and barn over a period of ~7 days, during each of the four seasonal sampling periods during the period June 2007 through April 2008. Continuous hydrogen sulfide (H_2S) measurements were made in-situ by using a pulsed fluorescence H_2S/SO_2 analyzer. During sampling, physiochemical and meteorological parameters were measured continuously. The two main RSCs identified by the GC-FID were dimethyl sulfide (DMS) and dimethyl disulfide (DMDS), which were found in almost every lagoon and barn sample. Overall average fluxes were 0.12 $\mu g\ m^{-2}\ min^{-1}$ for DMS, and 0.09 $\mu g\ m^{-2}\ min^{-1}$ for DMDS. These were approximately an order of magnitude lower than the overall average H_2S lagoon flux, which was 1.33 $\mu g\ m^{-2}\ min^{-1}$. DMS flux was found to be significantly influenced by lagoon pH, where as DMDS flux was significantly influenced by lagoon temperature. H_2S flux was significantly dependent on lagoon pH, lagoon temperature, and wind speed. For DMS and DMDS, the seasonal mean concentrations

ranged from 0.18-0.89 and 0.47-1.02 ppb, respectively. Seasonal mean H_2S barn concentrations were considerably higher ranging from 72-631 ppb. Barn H_2S concentrations were generally one to two orders of magnitude above their odor threshold. DMDS concentrations were also found to regularly exceed the lower limit of an odor threshold. The overall average barn normalized emission factors were 3.3 g day^{-1} AU^{-1} (AU (animal unit) = 500 kg) for H_2S, 0.018 g day^{-1} AU^{-1} for DMS and 0.037 g day^{-1} AU^{-1} for DMDS. RSC emissions from swine CAFOs in North Carolina were estimated to be 1.46 million kg yr^{-1} for H_2S, 9,509 kg yr^{-1} for DMS, and 17,406 kg yr^{-1}. H_2S swine CAFO emissions were estimated to contribute ~21% of North Carolina H_2S emissions.

3.1. INTRODUCTION

Reduced sulfur compounds emissions (RSCs) from concentrated animal feeding operations (CAFOs) can have a wide range of environmental impacts. On the local scale, the primary environmental effect is odor. RSCs are generally odorous, and are therefore key contributors to odorous emissions from CAFOs. Odor related emissions of compounds are important as they can cause health symptoms and additionally health effects (Schiffman and Williams, 2005). Furthermore they can affect the quality of life for people in surrounding areas (Wing and Wolf, 2000; Thu et al., 1997).

RSCs can also have regional environmental impacts as a result of the oxidation of reduced sulfur compounds, which leads to the formation of sulfur dioxide (SO_2). SO_2 can in turn further react to form aerosols such as ammonium sulfate and ammonium bi-sulfate. Particulate matter has a variety of environmental impacts; it can affect human health through inhalation of small particles, which can cause damage to the lungs (U.S. EPA, 1997), decrease visibility (Seinfeld and Pandis, 1998), and scatter incoming solar radiation, which can result in regional cooling (Lovelock et al., 1972).

Swine farming is one of North Carolina's largest animal agricultural industries, with approximately 2800 swine farm operations, and a swine population of ~ 10 million (United States Department of Agriculture (USDA), 2009). The majority of the pigs reside in the southeastern coastal plain of North Carolina. Of the swine farm operations, ~ 1600 have a thousand pigs or more (USDA, 2009). Therefore RSC emissions from waste at swine CAFOs in North Carolina are an issue of potential environmental concern.

H_2S is the most extensively studied of the RSCs. Concentrations and emissions of H_2S from swine CAFOs have been reported by a range of studies (Blunden and Aneja, 2008; Blunden et al, 2008; Jacobson et al., 2003; Jacobson et al., 2004; Heber et al., 2004; Zahn et al, 2001; Lim et al. 2003, Byler et al. 2004, Heber et al., 1997; Ni et al., 2002; Zhu et al., 2000; Kim et al., 2008). There is variance in both the concentrations and emissions reported due to different production, management and environmental conditions. However, the studies generally report H_2S concentrations 1-2 orders of magnitudes higher than their odor threshold, which is defined as the concentration of a chemical compound at which it's odor can first be detected.

In comparison to H_2S, other RSCs have not been studied as extensively. Currently, less than a handful of studies (Clanton and Schmidt, 2000; Blunden et al., 2005; Kim et al., 2007; Trabue et al., 2008) have reported concentrations of other RSCs at swine facilities. Results from these studies suggest that concentrations of these RSCs may exceed their odor threshold. Of these studies, none report anaerobic treatment lagoon emissions rates and only one reports barn emission rates, which was conducted in South Korea (Kim et al., 2007).

This chapter presents the measurement of RSCs emissions over four seasonal sampling periods, from both an anaerobic lagoon and barns at a swine CAFO in North Carolina. These emissions are evaluated with respect to seasonal variations and environmental parameters. Two different measurement techniques are used for measuring RSC emissions in this study. H_2S is determined continuously in-situ using a pulsed fluorescence analyzer. Other RSCs were collected using fused-silica lined (FSL) and

SUMMA polished stainless canisters and analyzed ex-situ using a gas chromatography-flame ionization detection (GC-FID) system.

In this chapter, H_2S emissions are presented to allow a comparison with other RSCs emissions, and to also determine their potential environmental impact. More in-depth analysis of H_2S emissions with respect to diurnal and seasonal variations, as well as meteorological and physiochemical factors are included in chapter II.

The potential environment impact of RSCs emissions from swine CAFOs are assessed by comparing concentrations to their odor threshold. Additionally, measured emissions are used to calculate the total North Carolina RSCs emissions from swine CAFOs.

3.2. METHOD AND MATERIALS

3.2.1. Sampling Site

The experimental site is an operational commercial swine finishing farm located in the eastern coastal plain of North Carolina, in Jones County. The farm consists of eight mechanically ventilated barns, with 900-1000 pigs placed in each barn.

The swine farm handles it's waste using a conventional method known as 'Lagoon and Spray Technology '(LST). In this method, the waste from the pigs fall through slatted floors into a shallow pit. The waste is flushed weekly through pipes into a water-holding structure, known as an anaerobic treatment lagoon. Waste from the anaerobic treatment lagoon can then be sprayed on surrounding crops as a source of nutrients. The waste from the anaerobic treatment lagoon waste is also recycled to flush

the barn pits. This method is employed by the majority of swine farms in North Carolina. Measurements of RSCs were from made from the anaerobic treatment lagoon and the barn.

3.2.2. Sampling Scheme

Measurements were made from the lagoon using a dynamic-flow through chamber system for a 5-7 day sampling period. For the barns, a sample line was placed directly in front of a ventilation fan. To calculate the flux, the flow rate from the barn was measured. The barn emissions were also measured for a 5-7 day period. Sampling was conducted over four seasons, the summer season from June 8th-June 28th, 2007; the fall season from the October 20th -November 12th, 2007; the winter season from February 8th-February 29th, 2008; and the spring season from 11th April-April 28th, 2008.

3.2.3. Field Sampling Technique and Instrumentation

3.2.3.1. Reduced Sulfur Compounds (RSCs)

RSCs were analyzed ex-situ using a GC-FID. The FID detects compounds with a hydrocarbon bond, which includes the RSCs of interest dimethyl sulfide (DMS; CH_3SCH_3), dimethyl disulfide (DMDS; $CH_3S_2CH_3$) and methyl mercaptan (CH_3SH).

3.2.3.1.1. Stability of RSCs in Canisters

Field sampling was conducted by collecting whole air samples. In this study, the whole air samples were collected using 6-L passivated canisters. Both SUMMA and fused-silica lined (FSL) canisters were used for sampling.

The SUMMA canister has an interior surface made of stainless steel, which is passivated by electrolysis and coated with a chrome-nickel oxide layer (Hsu et al., 2001). Humidified SUMMA canisters have been shown to be stable for a wide range of non methane volatile organic compounds (NMVOCs) for up to four weeks (Brymer et al., 1996; Ochiai et al., 2002). However, humidified SUMMA canisters are reported to be unsuitable for mercaptans (Brymer et al., 1996; Ochiai et al., 2002) including the sulfur compound of interest CH_3SH (Brymer et al., 1996). The stability of the other sulfur compounds of interest, DMS and DMDS, in humidified SUMMA canisters is uncertain, as there has been no known peer-reviewed study investigating the stability of these compounds.

FSL canisters are constructed of stainless steel in which a fused-silca coating has been added to the interior of the canister. Similarly, humidified FSL canisters are stable for a wide range of NMVOCs for up to four weeks (Ochiai et al., 2002). However, the fused-silca coating is applied to improve the recovery of RSCs. A recent study reported DMS and DMDS to have good recovery in humidified FSL canisters (Trabue et al., 2008). This study also found that CH_3SH had poor recovery in humidified FSL canisters. However, CH_3SH had good recovery in dry FSL canisters.

To assess the performance of the two types of canister in the recovery of DMS, DMDS and CH_3SH, a stability test was conducted. Individual gas cylinders of DMS (1 ppm), DMDS (1.05 ppm) and CH_3SH (10 ppm) mixed with nitrogen were obtained from Air Liquide (Houston, TX). Each gas was transferred using a syringe into pre-humidified SUMMA and FSL canisters. Canisters were pre-humidified by adding water into the

canister using a syringe. DMS and DMDS canisters were pre-humidified to a relative humidity (RH) of 32.4%. CH_3SH canisters were pre-humidified to 31.4% RH. Additionally, CH_3SH was injected into dry SUMMA and FSL canisters to observe the effects of varying moisture on recovery. The canisters were diluted using a high-purity nitrogen gas. The canisters were then analyzed over approximately a three-week period.

3.2.3.1.2. Field Sampling

Nine to eleven canister samples were taken from both the lagoon and barn over each measurement period. A mixture of 6-L SUMMA and FSL canisters were used for sampling. Of these, approximately a quarter were FSL canisters. Prior to sampling, the canisters were cleaned by a XonTech Model 960 canister cleaning system. The automated system performs a cycle of cleaning, where canisters are evacuated, filled with humidified air and then baked at 120^{o}C. The canisters were cleaned using 2 cycles. After the cleaning, the system evacuates the canisters to < 0.05 mm Hg using a vacuum pump.

Samples were taken over a period of ~5 minutes at different times of the day (between 8:00 and 18:00 EST) and in different meteorological conditions to examine the factors that influence RSCs emissions. A summary of the time and frequency of canister sample collection is provided in Table 3.1. Samples were collected over a minimum of four days over each lagoon and barn sampling period.

3.2.3.1.3. Analytical System

Analysis of the canisters was conducted at the National Exposure and Research Laboratory (NERL) of the US Environmental Protection Agency (EPA) in Research Triangle Park, NC. Samples were analyzed using a Hewlett-Packard Model 5890A

(Avondale, CA) gas chromatography system. The system includes a cryogenic u-shaped stainless steel trap, which is used to pre-concentrate the sample using liquid argon (-187^{o}C). The sample is drawn onto the cryogenic trap, which is immersed in liquid argon, the trap is then immersed in a dewar of boiling water (~99^{o}C). The sample is then separated using a J & W Scientific (Folsom, CA) DB-1 column (60m x 0.32mm x 1 μm). Helium carrier gas is kept at a constant pressure of 150kPA. At 75^{o}C, this provides a flow rate of 2.65 cm^{3} min^{-1}. The initial column temperature is -50^{o}C, this temperature is held for two minutes, and then increases at a rate of 8^{o}C/min to 200^{o}C. The temperature is then held at 200^{o}C for 7.75 min, before a further temperature increase of 25^{o}C/min to 225^{o}C. Finally the temperature is held at 225^{o}C for 8 minutes. The FID applies a voltage of 200v and was maintained at a temperature of 275^{o}C. The flow rates for hydrogen and air were 48 and 325 cm^{3} min^{-1}, respectively, with a make-up gas of 30cm^{3} min^{-1} of nitrogen.

Calibration of the GC-FID system was performed using 0.25 ppm ± 1.2% propane in air (National Institute of Standards and Technology Standard Reference Material). From the slope of the multi-point calibration curve, a response factor is determined based on ppbC (parts per billion carbon) area^{-1}. This is applied to all observed peaks. The FID has a uniform carbon response for all peaks, therefore a single response factor can be used to represent all compounds (Blades, 1976; Sternberg et al., 1962). Additionally a 4 compound standard cylinder containing Ethane (48.7ppb), Propane (53.9 ppbC), Isobutane (51.2ppb), and n-Butane (54.6 ppbC) is used regularly to provide verification of retention time location, and FID response. For quality assurance and quality control, the analytical reproducibility is tested by repeat analysis of samples. The data integration

system is performed using the ChromPerfect-5890 Direct chromatographic software program (Justice Innovations, Mountain View, CA). A different software program known as HCID (Graham Solutions, Conyers, GA) is used to check the integration, and manually re-integrate as necessary. This software also allows the use of a file named CALTABLE, which contains approximately 300 compounds retention times, retention index and compound name including the RSCs, DMS, DMDS and CH_3SH. To convert from ppbC to ppb, a compound is adjusted using it's effective carbon number (Scanlon and Willis, 1985; Kallai and Balla, 2002; Jorgensen et al., 1990). The limited information available suggests that sulfur has no effect on FID response (Jorgensen et al., 1990).

In order to confirm the accuracy of the peak naming procedure or to identify unknown compound peaks a gas chromatography-mass spectrometry (GC/MS) system is used. The analytical instruments are a Hewlett-Packard Gas Chromatograph Model 6890 combined with a Hewlett Packard Model 5972 Mass Selective Detector. The same column, temperature program, and pre-concentration system is used for the GC-MS as the GC-FID. A difference between the systems is the use of an electronic pressure control device to keep the helium carrier flow rate constant at 1.4 cm^3/min, throughout the temperature program. This occurs due to pressure changing with column temperature. At 75^oC, the pressure is measured as 67 kPa.

3.2.3.2. Hydrogen Sulfide (H_2S)

A Model 450C pulsed fluorescence H_2S/SO_2 analyzer with a range of 0-1000 ppb was used to measure H_2S concentrations continuously in-situ. A multi-point calibration was conducted for the analyzer before each experimental period, using a TEI model 146

dilution-titration system (Thermo Environmental Corporation, Mountain View, CA). Additionally the instruments were zeroed and spanned regularly during the sampling period. This procedure was also performed after each sampling period. SO_2 concentrations were not considered for analysis, as concentrations were found to be negligible at the swine CAFO.

3.2.4. Lagoon, Barn and Environmental Parameter Measurements

A brief summary of the most pertinent information regarding the lagoon, barn and environmental parameter measurements methodology are presented in this chapter. Further details on the methodology are described in chapter II.

3.2.4.1. Lagoon Measurements

A dynamic flow-through chamber system was used to determine anaerobic lagoon flux (Blunden and Aneja, 2008; Aneja et al., 2000).

Compressed zero-grade air (Machine and Welding Supply Company, Raleigh, NC) flows into the chamber through Teflon tubing. The flow rate was set to ~ 4 L min^{-1} for H_2S measurements, and 4-6 L min^{-1} for lagoon canister samples. Inside the chamber, a rotating Teflon impeller was used to ensure that the air is well mixed similarly to ambient air. The steady state flux was calculated using the following equation:

$$J = [C\ ]\left[\frac{q}{V}\right]h \qquad (1)$$

where, J is the compound flux, q is the flow rate of carrier gas through chamber, C is the concentration of compound in carrier gas, V is the volume of chamber above the lagoon surface, and h is the height of the chamber.

3.2.4.2. Barn Measurements

Barn measurements were made at one of the eight swine barns at the sampling site. At the west end of the barn facing the lagoon there are five fans, that turn on in a set sequence, as the temperature increases inside the swine barn.

The equation used to calculate the barn flow rate is determined as the following:

$$Calculated\ fan\ flow\ rate = Manufactures\ fan\ flow\ rate \times \left(\frac{Measured\ RPM}{Specified\ RPM}\right) \quad (2)$$

The measured flow rate of the fans was determined using a rotation-voltage relationship system (Blunden et al., 2008). Motors were attached to the fans, that produced a voltage when the fans were rotating. Measurements of the static pressure difference between the inside and outside of the building were made. The manufacturers fan flow rate was adjusted for the average static pressure measurement. During canister sampling, fan voltages were recorded and used to calculate the ventilation rate at the time of sampling.

To calculate the emission rate from the swine barn, a sample line was placed directly in front of the first fan to turn on. The concentration distribution was assumed to be uniform across the fan. Concentrations were also assumed to be equal for all five fans.

For the H_2S/SO_2 analyzer, background samples were collected upwind of the barns using FSL canisters. Concentrations were negligible in comparison to

corresponding H_2S concentration measured from the ventilation fan, therefore they were not considered during emission calculations. For other RSCs, background canister samples were taken simultaneously to the barn samples. The samples were collected upwind of the swine house, and were analyzed identically to the barn canister samples. No RSCs were identified in background samples.

The barn emission rates were calculated using the following equation:

$$J = C * \sum f \quad (3)$$

where J is the compound flux, C is the gas concentration at the fan, $\sum f$ is the sum of the flow rates of each individual fan.

3.2.4.3. Environmental Parameter Measurements

Meteorological and physicochemical factors can have a significant effect on emissions from a swine farm. Therefore meteorological parameters, i.e. relative humidity, air temperature, and solar radiation were measured at a height of 2 m. Additionally, wind speed and wind direction were measured at a height of 10 m. Lagoon physicochemical factors were also measured. Lagoon temperature and pH were measured continuously at a depth of ~7cm. Also, near-surface (< 10 cm) anaerobic treatment lagoon samples were taken daily to be analyzed for sulfide content. For barn sampling, temperature was continuously measured at the fan outlet.

3.3. RESULTS

3.3.1. Stability Test

DMS, DMDS and CH_3SH stability are presented in Figure 3.1. Results show that DMS and DMDS exhibit excellent recovery over a three-week period for both humidified SUMMA and FSL canisters with their recovery over the entire period ± 4%.

CH_3SH recovery was poor for SUMMA canisters. In the humidified SUMMA canister, CH_3SH was not detected after two days. For the dry SUMMA canister, CH_3SH was not initially detected, and is therefore not included in the figure. This supports the findings of Brymer et al. (1996). Brymer et al. (1996) investigated stability of various compounds including CH_3SH in humidified SUMMA canisters. At the first examination of recovery after seven days, methyl mercaptan was found to be below the limit of detection.

The FSL canisters results show that the dry FSL canister had better CH_3SH recovery than the humidified FSL canister. The dry FSL canister had an excellent recovery of ± 5% for up to eight days. After this time, the recovery began to decrease. By 23 days the recovery was 60%. In comparison, the humidified FSL canister had reduced recovery, with a recovery of 80% over two days, 45% over eight days and 8% over 23 days. These results are supported by a study conducted by Trabue et al., (2008). Their study reported a 60% recovery of CH_3SH after 4 hours in humidified FSL canisters and ~100% recovery in dry canisters after 4 days.

Results from this study indicate that water content increases the stability of CH_3SH in SUMMA canisters, and decreases CH_3SH stability in FSL canisters. The effect of

water content on CH_3SH in FSL canisters contrast with how NMVOCs usually behave in stainless steel canisters. Typically humidity improves the stability of compounds, as water molecules occupy active sites on the canister surface.

The results suggest that the stability of DMS and DMDS in SUMMA and FSL canisters will not effect measured concentrations. In contrast, the experiment indicates that CH_3SH will not be measured in SUMMA canisters, and may be at reduced concentrations in FSL canisters

3.3.2. RSCs Emissions

The two main RSCs identified in this study were DMS and DMDS, which were identified in almost every lagoon and barn sample. CH_3SH was not identified in any lagoon or barn samples, despite many FSL canisters being analyzed within an appropriate time. Therefore, it is hypothesized that a combination of low concentrations and instability, resulted in CH_3SH not being detected. Furthermore, CH_3SH may convert to DMDS in the canister. Additionally, dimethyl trisulfide ($CH_3S_3CH_3$) was identified by the GC-FID in some lagoon and barn samples. However, the compound concentration was around the detection limit and was therefore not selected for further analysis.

The GC-MS additionally identified carbon disulfide (CS_2) in samples, but for this study, the GC-MS was not used to quantify compounds.

The RSCs emissions results presented in this paper include continuously measured H_2S. However, it should be noted that H_2S emissions are only presented to allow a comparison with other RSCs emissions, and to also determine their potential

environmental impact. More in-depth analysis of H_2S emissions with respect to diurnal and seasonal variations, as well as meteorological and physiochemical factors are included in chapter II. Additionally, chapter II discusses measured H_2S emissions in comparison to previous swine CAFO studies.

3.3.2.1. Lagoon Fluxes

Table 3.2 and Table 3.3 present the RSCs fluxes and their corresponding environmental parameters from the anaerobic lagoon. It should be noted that for DMDS, there may be possible system peak interference on two samples. Therefore these samples were excluded from analysis. As mentioned, canister samples were collected during the daytime. As observed for H_2S lagoon flux in chapter II, there is diurnal variation in lagoon fluxes, therefore the flux values presented for DMS and DMDS are not representative of a full day as they do not take into account nighttime variations in flux. The sampling period(s) during the day also represented a short sampling period (Table 3.1) and this should be considered when using the estimated flux values.

DMS and DMDS seasonal fluxes (Table 3.2) are both highest in the summer sampling season, with DMS flux slightly higher than DMDS flux, 0.26 compared to 0.22 $\mu g\ m^{-2}\ min^{-1}$, respectively. DMS flux is slightly higher in all seasons apart from spring, where the DMDS flux is 0.11 $\mu g\ m^{-2}\ min^{-1}$ compared to DMS flux of 0.06 $\mu g\ m^{-2}\ min^{-1}$. DMS seasonal flux is 2nd highest in the fall and 3rd highest in the spring. This trend is reversed for DMDS seasonal fluxes. DMS and DMDS have their lowest fluxes in winter

with values of 0.05 and 0.02 μg m^{-2} min^{-1}. The overall average fluxes are 0.09 μg m^{-2} min^{-1} for DMS, and 0.12 μg m^{-2} min^{-1} for DMDS.

There are no known previous swine CAFO measurements of DMS and DMDS lagoon fluxes to compare the values in this study to. DMS and DMDS seasonal fluxes are lower than H_2S fluxes in all seasons (Table 3.3), particularly in the summer and fall season, where they are an order of magnitude lower. However, the winter flux is only marginally lower than the H_2S average winter flux of 0.08 μg m^{-2} min^{-1}. For H_2S, which is continuously collected over a 5-7 day period, the highest flux is in the summer season with a flux of 3.81 μg m^{-2} min^{-1}. This is almost three times higher than the fall flux (1.17 μg m^{-2} min^{-1}), and at least an order of magnitude higher than both the spring (0.27 μg m^{-2} min^{-1}) and winter flux (0.08 μg m^{-2} min^{-1}). The overall average flux for H_2S is over an order of magnitude higher than for DMS and DMDS with a flux of 1.33 μg m^{-2} min^{-1}.

The relationship between RSC fluxes was investigated by using the coefficient of determination (r^2). Figure 3.2 presents the relationship between the three RSCs. All three compounds exhibit strong correlation. The strongest relationship is between H_2S and DMDS with a r^2 value of 0.61 ($p<0.0001$), then H_2S and DMS with a r^2 value of 0.43 ($p<0.0001$). DMS and DMDS have the lowest coefficient of determination with a r^2 value of 0.36 ($p<0.0001$). Examination of Figure 3.2 shows that DMS has a weaker relationship than DMDS with H_2S primarily as the result of the presence of an outlier for DMS in the summer season. This does not occur for DMDS as it has a corresponding high flux value. The DMS and DMDS relationship seems the weakest largely due to the fall values, where

DMS flux is considerably higher than DMS flux. These differences are possibly the result of the compounds response to environmental factors, which is discussed in the next section.

3.3.2.1.1. The Influence of Environmental Parameters on RSCs Lagoon Fluxes

The influence of environmental parameters on DMS and DMDS fluxes was statistically analyzed using r^2, and their respective p-values. Air temperature was included in this analysis, as the effect of dynamic-flow through chamber system on air temperature is minimal. Arkinson, (2003) using this chamber system for flux measurements, determined the air temperature difference between the outside and inside of the chamber to be $1.55 \pm 2.30\ ^{o}C$.

The results of this analysis are shown in Table 3.4. For both DMS and DMDS, there were three environmental parameters that were found to have a significant correlation ($p<0.05$). These were pH, lagoon temperature and air temperature. Figure 3.3 and Figure 3.4 show that lagoon temperature and pH have opposite effects for both DMS and DMDS, with flux increasing with decreasing pH, and increasing with lagoon temperature. Air temperature showed a similar trend to lagoon temperature for DMS and DMDS flux. To determine which environmental parameters influence flux, multiple linear regression was performed using SAS (Statistical analysis software v8, Cary, NC). The analysis found that pH was the only significant factor influencing DMS flux. For DMDS, the analysis found only lagoon temperature to be a significant factor. Ambient temperature was not found to be a significant parameter in influencing DMS or DMDS flux. It is hypothesized that the correlations observed were the result of ambient temperatures

relationship with lagoon temperature. In comparison, statistical analysis found H_2S fluxes to be dependant on lagoon pH, lagoon temperature and air temperature (see chapter II).

Lagoon pH was found to be the significant factor in effecting DMS, with emissions increasing with decreasing pH. For this to occur there has to be dissociation of DMS. However there are no known studies discussing the aqueous dissociation of DMS. It should also be noted that although pH was found to be the only statistically significant factor effecting fluxes, lagoon temperature was found to be significantly correlated with DMS fluxes, and had an r^2 value only 0.03 lower than lagoon pH. Therefore it is suggested that further measurements would help to confirm the effects of lagoon temperature and lagoon pH on DMS lagoon fluxes.

DMDS fluxes were found to be significantly influenced by lagoon temperature, with fluxes increasing as lagoon temperature increases. This effect can be explained by changes in the mass transfer coefficient, as an increase in lagoon temperature can increase the mass transfer of gases across the air-manure interface (Arogo et al., 1999). Additionally, an increase in lagoon temperature can increase microbial activity, resulting in increased rates of decomposition, thus increasing the amount of sulfide available.

In this study, the relationship between anaerobic treatment lagoon sulfide content and RSC fluxes could not be determined. This was the result of ~two-thirds of the sulfide samples collected being below the analytical detection limit of 1 mg L^{-1}. Therefore there was not enough data available to perform accurate statistical analysis.

3.3.2.2. Lagoon Emissions

The lagoon emissions for the swine CAFO were calculated based on the lagoon surface area at the time of sampling. The surface area of the lagoon was measured manually for one season. For the other seasons, the lagoon surface area was adjusted from the measured surface area based on the relative liquid lagoon level and the slope ratio. Using the lagoon surface area and the average flux for each season, seasonal lagoon emissions were calculated. These values are presented in Table 3.5. Lagoon surface area was the smallest in the summer and fall seasons with an area of 17,702 m^2. In the winter, the lagoon surface area had increased by ~4% to 18,372 m^2. This trend continued with a further ~2% rise in the spring season, resulting in a lagoon surface area of 18,802 m^2.

DMS emissions ranged from 1.32-6.63 g day^{-1} with an overall average emission of 3.09 g day^{-1}. DMDS lagoon emissions were slightly lower, ranging from 0.53-5.61 g day^{-1} with an overall average emission of 2.54 g day^{-1}. H_2S seasonal emissions were at least an order of magnitude higher than DMS and DMDS emissions. H_2S lagoon emissions varied from 2.12-97.1 g day^{-1}, with an overall average emission of 34.1 g day^{-1}. As the lagoon surface area only varied 6% throughout all the sampling seasons, the seasonal emission trends were similar to the seasonal flux trends.

3.3.2.3. Barn Concentrations and Emissions

RSCs concentrations, ventilation rates, emission rates and corresponding environmental parameters are presented in Table 3.6 and Table 3.7. Similarly to lagoon samples, it should be noted that canisters sampling was conducted during the daytime. In chapter II, diurnal variations in H_2S barn concentrations and emissions can be observed.

Therefore the barn concentrations and emissions for DMS and DMDS are not representative of a full day as they do not take into account nighttime variations in emissions. Also, the sampling period(s) during the day represented a short sampling period (Table 3.1) and this should be considered when using the estimated concentration and emission values.

DMS and DMDS concentrations ranged from 0.18-0.89 ppb and 0.47-1.02 ppb, respectively (Table 3.6). The highest average seasonal concentrations both occurred in the fall season. Similarly, the lowest average seasonal concentrations both occurred in the summer season. DMS average concentration was higher than DMDS in the winter and spring. Conversely, DMDS average concentration was higher than DMS in the summer and fall. The highest individual DMS concentration was 2.09 ppb, which occurred in the fall season. The highest individual DMDS concentration occurred in the spring season with a value of 1.69 ppb. DMS and DMDS concentrations from the barn were 2-3 orders of magnitude lower than H_2S concentrations. The highest H_2S average seasonal concentration is 631 ppb, which occurs in spring (Table 3.7.). This average concentration is actually higher than reported as a result of 27% of the data going beyond the detection limit of a 1000 ppb. The next highest is the fall season (327 ppb), followed by the winter (164 ppb) and summer (72 ppb), respectively.

To further investigate RSCs concentrations, the relationships between DMS, DMDS and H_2S barn concentrations were analyzed using the co-efficient of determination (r^2). Figure 3.5 presents this analysis. The relationship between sulfur compounds concentrations is not particularly strong. The strongest occurs between DMS

and H_2S ($r^2 = 0.20$; $p = 0.0050$), then DMS and DMS ($r^2 = 0.13$; $p = 0.0283$). The relationship between DMDS and H_2S is very weak ($r^2 = 0.03$; $p = 0.2868$).

The weak relationships between DMS and H_2S, and DMDS and H_2S seem to occur as a result of the spring sampling season, where comparatively H_2S concentrations are considerably higher. The poor relationship between DMS and DMDS seem to result from variability in comparative concentrations in all sampling seasons.

Table 3.8 presents DMS and DMDS barn concentrations from previous swine CAFO studies. Blunden et al. (2005) took samples from in front of a barn fan at the same sampling site as this study, during two different sampling seasons, and measured average concentrations of DMS and DMDS ranging from 0.1-0.2 ppb, which is lower than the average concentrations observed in this study. Samples were also taken from a finishing farm in North Carolina with natural ventilation. At this swine CAFO, concentrations were found to range from 0-1.6 ppb for DMS and 0-0.2 ppb for DMDS.

Concentrations in this study are lower than those reported by a Kim et al. (2007) study in South Korea. They made measurements of sulfur compounds concentrations and emissions from mechanically ventilated swine operations. They reported individual concentrations ranging from 1.5-12 ppb for DMS and 0.5-7 ppb for DMDS for five different facility types; these were gestation, farrowing, nursery, growing and fattening/finishing. Mean concentrations ranged from 2.1-8.4 and 0.9-4.7 ppb for DMS and DMDS, respectively. The finishing facility was found to have the highest mean concentrations out of the five facility types. It is noted though that all the facility types

employed a deep pit manure collection system, which tends to store manure longer than shallow pit systems, resulting in increased emissions.

Clanton and Schmidt (2000) made measurements of RSCs in a variety of different manure collection systems. Air samples were taken from commercial Minnesota swine operations and a simulated deep pit system, which contained manure from a swine gestation/farrowing/nursery facility. For the simulated deep pit system, concentrations ranged from 2.2-5.1 ppb for DMS and 0-3.9 ppb for DMDS. For a pit fan sample taken at a deep pit gestation facility, a DMS concentration of 2.2 ppb was measured; DMDS though was not detected. Additionally, DMS and DMDS were not detected in any of the nursery pull plug facilities air samples.

Trabue et al. (2008) also measured RSC concentrations from different manure management systems. Samples taken from the pit fan of a deep pit system had an average DMS concentration of 5.3 ppb. In the same samples, DMDS was measured below the limit of quantification. In samples taken from pull plug manure collection systems in finishing and farrowing facilities neither DMS or DMDS were detected.

Overall, taking into account the variations in ventilation system, manure collection system, sample location, season and climate, the measured concentrations in this study compare well, as the concentrations are in the same order of magnitude as previous swine CAFO studies.

The seasonal DMDS emission rates were higher for all four seasons in comparison with DMS (Table 3.6). DMDS highest emission rate was in the summer (4.25 g day^{-1}). The lowest emission rate was in the winter with a value of 1.41 g day^{-1}.

DMS emissions ranged from 0.90 g day^{-1}, which was measured in the summer to 2.17 g day^{-1}, which was measured in the fall. Seasonal barn emission rates for DMS and DMDS were two to three orders of magnitude higher than H_2S emission rates. H_2S highest emission rate occurred in the spring with a value of 647 g day^{-1} (Table 3.7). Fall and summer were next highest, 206 g day^{-1} and 189 g day^{-1}, respectively. The lowest emission rate occurred in the winter (79.8 g day^{-1}).

Animal weight is one of the largest factors influencing emissions from a barn. Therefore seasonal emissions were normalized by 500 kg of live animal weight (LAW), also known as 1 animal unit (AU). The LAW and the corresponding pig production numbers as well as the normalized RSC seasonal emissions are shown in Table 3.9. The average seasonal normalized emissions are also presented.

Normalized seasonal emissions for DMS and DMDS ranged from 0.010-0.032 and 0.013-0.061 g day^{-1} AU^{-1}, respectively. Both compounds had their highest normalized seasonal emissions in the fall. Lowest normalized seasonal emissions occurred in the winter for DMDS. DMS had equally lowest emissions in the summer and winter seasons. DMDS overall average normalized barn emission (0.037 g day^{-1} AU^{-1}) is approximately twice as high as the emission for DMS (0.018 g day^{-1} AU^{-1}).

DMS and DMDS normalized seasonal emissions are significantly lower than H_2S. The highest seasonal H_2S emission is in the spring season with an emission of 7.31 g day^{-1} AU^{-1}. Fall and summer sampling seasons are the next highest with emissions of 2.99 and 2.20 g day^{-1} AU^{-1}, respectively. The lowest emission occurred in winter with a value

of 0.72 g day^{-1} AU^{-1}. The overall average H_2S emission is two orders of magnitude higher for H_2S (3.3 g day^{-1} AU^{-1}) compared to DMS and DMDS.

RSCs emissions were further investigated by examining the relationships between DMS, DMDS and H_2S barn normalized emissions (Figure 3.6.). Similarly to the barn concentration analysis, the strongest relationship was between H_2S and DMS ($r^2 = 0.28$, $p = 0.0007$), and the weakest between H_2S and DMDS ($r^2 = 0.03$, $p = 0.2852$). DMS and DMDS were slightly better correlated with an r^2 value of 0.18 ($p = 0.0075$). As with the H_2S and DMS concentration relationship, the H_2S and DMS emission relationship was effected by high H_2S emissions in the spring season in comparison to DMS emissions. High H_2S emissions in the spring and fall in comparison to DMDS emissions were mostly responsible for the corresponding weak relationship. The poor relationship between DMS and DMDS was influenced by variability in comparative emissions in all seasons.

The variance in RSCs emissions is caused by a range of factors. One of the most important is the total amount of sulfide in the barn, which is a product of the total amount of manure in the barn, and the % sulfide content of the manure. In this study, the total amount of manure in the barn was taken into account by normalizing the emission rate by 500 kg of live animal weight. However, there are other factors related to manure management such as flushing frequency and the amount of time since the barn was cleaned that influence the total amount of manure in the barn. The % sulfide content of the barn manure can also be variable. The % sulfide content is determined by the sulfur content of the feed, and the efficiency of the pig in retaining sulfur.

Also important in causing variance in emissions are environmental conditions that influence the release of gases from manure. In this study, barn temperature was measured. Increases in barn temperature will result in increases in manure temperature, which as discussed will increase gas emissions. DMS and DMDS emissions were found to have very weak relationships with barn temperature. The r^2 values were 0.05 ($p = 0.1607$) and 0.05 ($p = 0.1538$), for DMS and DMDS, respectively. However, the r^2 value for DMS was for a negative correlation. The weak correlations were the result of variability in the relationship in all seasons. H_2S barn emissions were found to have a stronger correlation with barn temperature ($r^2 = 0.19$, $p< 0.0001$), (see chapter II). The relationships might be stronger, if the emissions were correlated with manure temperature. However, it was beyond the scope of the study to measure this environmental parameter and others such as manure pH, and the speed of the air movement across the manure surface.

A further reason that the relationship between RSC barn emissions and barn temperature is not stronger is that barn emissions are not just dependant on environmental parameters, but are additionally related to the past emission patterns, which control the mass of a gaseous compound in the barn at a given moment in time. The amount of a gaseous compound in the barn is a function of two processes. Firstly, the total amount of the gaseous compound being produced by the manure over a given time, which is influenced by environmental factors and secondly, the total amount of a gaseous compound leaving the barn over a given time, which is controlled by the ventilation rate. Therefore, if the amount of a RSC exiting the barn through fan ventilation is greater than

the amount of a RSC being emitted from the manure, or conversely if the amount of a RSC exiting the barn through fan ventilation is less than the amount of the RSC being emitted from the manure, then the RSCs barn emissions are in an unsteady state. This unsteady state can result in the amount of a RSC in the barn either increasing or decreasing with time. The more unsteady or unbalanced the relationship between these processes, the weaker the influence of environmental parameters on emissions. It is hypothesized that this imbalance of barn inputs and outputs result contributed to the weak influence of barn temperature on RSC emissions observed in this study.

In comparison to the only other known study reporting RSCs emission rates, the measured DMS and DMDS emissions in this study are an order of magnitude lower. Kim et al. (2007) study in South Korea, calculated normalized emissions ranging from 0.22-0.94 g $day^{-1}AU^{-1}$ for DMS and 0.12-0.53 g $day^{-1}AU^{-1}$ for DMDS, for five different types of pig production stages. It is expected that this difference in emissions is caused by the different production, management and environmental conditions.

3.3.3. Potential Environmental Impacts

3.3.3.1. Odor

A potential environmental impact of RSC swine CAFO emissions is the effect of odor on the health of the local surrounding population who reside nearby. Chemical compounds are odorous when they exceed their odor detection threshold, which is defined as the lowest concentration of a chemical compound that produces a sensory response in the olfactory receptors of humans (American Industrial Hygiene Association,

(AIHA), 1989). In odor testing, it is defined as the minimum concentration of sensory response detected in 50% of the odor panel (AIHA, 1989). Odorous compounds can cause health symptoms and health effects even it is below an irritant threshold (Schiffman and Williams, 2005). This occurs because unpleasant odors can cause a change in the functioning of the human brain and body as a result of a biological response (i.e. the human nervous system reacts to bad odors to warn us against potentially unsafe air and food), which in turn can lead to the developments of health symptoms and health effects (Schiffman and Williams, 2005). RSCs are of particular concern as they have unpleasant odors and low odor thresholds. Schiffman and Williams (2005) identified six community studies where exposure to low concentrations of H_2S or RSCs have been related to health effects. In two of these studies, health effects were reported from an average daily H_2S concentration exposure of 10-11 ppb.

A summary of H_2S, DMS, and DMDS odor thresholds and characteristics available in literature are presented in Table 3.10. It can be observed that there is slight variance in the reported odor thresholds. This is due to the studies using different literature sources and methodologies to calculate the mean odor threshold. The RSCs all have low odor thresholds, with odor thresholds ranging from 4.5-17.8 ppb for H_2S (American Industrial Hygiene Association (AIHA), 1989; Devos et al., 1990; Amoore and Hautala, 1983), 2.24-20 ppb for DMS (Devos et al., 1990; Haz-Map, 2009) and 0.78-12.3 ppb for DMDS (Devos et al., 1990; Haz-Map, 2009). A comparison of H_2S barn concentrations to their odor thresholds is presented in Table 3.11. It can be observed that the average seasonal concentrations are considerably higher than the odor thresholds. Of

the 2415 15 minute average data points recorded in this study, only two did not exceed all of the odor thresholds. These concentrations occurred in the summer and winter sampling seasons and are respective minimums in each of the seasons. However, it should be noted that these concentrations did exceed the lowest two odor thresholds. The highest peak concentrations occurred in the spring season with 27 % of the 15 minute average data points above the limit of detection of the analyzer, which was 1000 ppb. Peak concentrations were 197, 796 and 345 ppb for the summer, fall and winter seasons, respectively. These peak concentrations are all at least an order of magnitude higher than the odor thresholds. The extent that 15 minute concentrations exceed their odor threshold was assessed by determining the number of 15 minute data points that were at least an order of magnitude higher than the average of the three odor thresholds, which was 101.3 ppb, (Table 3.11). This was highest in the spring with 97% of 15 minute average concentrations above 101.3 ppb. The next highest were fall and winter with 93% and 79% of 15 minute average concentrations above 101.3 ppb. The season with the least amount of 15 minute concentrations above 101.3 ppb was spring with 27%.

A comparison of DMS and DMDS barn concentrations to their odor threshold is summarized in Table 3.12. No DMS concentrations exceed their odor thresholds, with the highest individual concentration in fall (2.09 ppb) just below the lowest odor threshold of 2.24 ppb. Individual DMDS sample concentrations exceeded the lowest odor threshold in all sampling seasons (0.78 ppb). The fall had the most samples exceeding this odor threshold with eight, however the spring had the highest individual concentration of 1.69

ppb. Fall was the only season where the average seasonal concentration (1.02 ppb) exceeded the lowest odor threshold.

From this analysis, it can be concluded that H_2S concentrations are most likely to cause odor related health effects. It is though beyond the scope of this study, to model the dispersion of H_2S from swine CAFOs to predict downwind concentrations of H_2S. However it is of interest, that the diurnal profile of barn concentrations in chapter II show that concentrations tend to be highest during the night, when there is a shallow planetary boundary layer.

3.3.3.2. North Carolina RSC Emissions

The potential environmental effect of RSC swine CAFO emissions on a regional scale can be evaluated by calculating the total North Carolina swine CAFO emissions. To achieve this, the overall average fluxes for the RSCs were used. These were 1.33 $\mu g\ m^{-2}\ min^{-1}$ for H_2S, 0.12 $\mu g\ m^{-2}\ min^{-1}$ for DMS and 0.09 $\mu g\ m^{-2}\ min^{-1}$ for DMDS. In addition, the total swine CAFO lagoon area in North Carolina was determined. Aneja et al., (2000) estimated that the average size of a lagoon is ~1 ha (10,000 m^2), using a SPOT satellite image of North Carolina. In 2007 (most recent data available), it was estimated that the number of swine CAFOs in North Carolina was 2,800 (USDA, 2009). Using this information and the overall average flux, the North Carolina RSC lagoon emissions were estimated as 18,175 kg yr^{-1} for H_2S, 1640 kg yr^{-1} for DMS and 1230kg yr^{-1} for DMDS.

The North Carolina barn emissions were calculated using the most recent statistics ((December, 2008-February, 2009 period) provided by the USDA (USDA,

2009). Information was provided on the population and weight of North Carolina pigs. The swine population was divided into five weight classes. These classes were breeding, under 60 lbs, 60-119 lbs, 120-179 lbs, and over 180 lbs. A weighted average was calculated using the amount of pigs in each class. For the breeding class the average weight was estimated to be 433 lbs (Williams, 2005). For >180lbs, 220 lbs was estimated to be the average weight. It was determined that the under 60 lbs category represented feeder pigs, which are estimated to have an average weight of 30 lbs (Williams, 2005). For the remaining two classes the average of the class weight range was used i.e. 90 and 150 lbs, respectively. From this, the total live animal weight for North Carolina pigs was calculated, which is presented in Table 3.13.

The RSC overall average barn emissions were used as emission factors. From Table 3.9, these are the following: 3.3 g day^{-1} AU^{-1} for H_2S, 0.018 g day^{-1} AU^{-1} for DMS, and 0.037 g day^{-1} AU^{-1} for DMDS. These were applied to all classes of animal weight. From this, the total RSC barn emissions were estimated. Results show that barns at North Carolina swine farms emit 1.44 million kg yr^{-1} of H_2S. Statewide estimates of DMS and DMDS are significantly lower, 7,870 kg yr^{-1}, and 16,176 kg yr^{-1}, respectively. North Carolina H_2S barn emissions are two orders of magnitude higher than lagoon emissions. For DMS and DMDS, barn emissions are not as dominant, with lagoon emissions contributing ~17% and ~7%, respectively. Total emissions from North Carolina swine CAFOs (barn + lagoon) are therefore 1.46 million kg yr^{-1} for H_2S, 9,509 kg yr^{-1} for DMS, and 17,406 kg yr^{-1} for DMDS.

The North Carolina Division of Air Quality (NCDAQ) released an North Carolina H_2S emission inventory for 2002 stating total emissions of 5.40 million kg yr^{-1} (NCDAQ, 2003). This inventory did not include emissions from animal operations. By adding the contribution of the swine farms to the inventory, it is therefore estimated that H_2S emissions from swine barns and lagoons in North Carolina comprise approximately 21% of statewide H_2S emissions.

3.4. CONCLUSIONS

Measurements of RSC emissions were made from an anaerobic lagoon and barn at a swine CAFO in North Carolina. These emissions were evaluated with respect to seasonal and environmental factors. Furthermore, the potential environmental impact of RSC emissions was assessed by comparing barn exhaust concentration to their odor threshold and by estimating total North Carolina RSC emissions.

RSCs apart from H_2S were analyzed ex-situ using a combination of SUMMA and FSL canister and a GC-FID system. Stability tests found good recovery of DMS and DMDS in humid SUMMA and FSL canister. However, CH_3SH had moderate recovery in humid FSL canisters and very poor recovery in humid SUMMA canisters. In sampling analysis, DMS and DMDS were found in almost every lagoon and barn sample. CH_3SH though was not identified in any lagoon or barn sample.

Overall average DMS and DMDS lagoon fluxes were over an order of magnitude lower than H_2S fluxes, 0.12 and 0.09 μg m^{-2} min^{-1} compared to 1.33 μg m^{-2} min^{-1}, respectively. RSC fluxes were statistically analyzed and found to be significantly

influenced by different environmental parameters. DMS flux was significantly influenced by pH, where as DMDS was significantly influenced by lagoon temperature. H_2S was found to influenced by pH, lagoon temperature and wind speed.

The overall average barn emissions for DMS and DMDS were 0.018 g day^{-1} AU^{-1} and 0.037 g day^{-1} AU^{-1}, respectively. These were approximately two orders of magnitude less than the overall average H_2S normalized seasonal emission factor for barns, which was 3.3 g day^{-1} AU^{-1}. The relationships between RSC barn concentrations and emissions were found to be weaker than the relationship between RSC lagoon fluxes. RSC emissions did not correlate well with barn temperature, particularly for DMS and DMDS.

H_2S barn concentrations were found to exceed four different published odor thresholds by one to two orders of magnitude. No DMS concentrations exceeded their odor threshold. DMDS concentrations were found to regularly exceed the low limit of the Haz-Map, (2009) odor threshold.

Using the overall average flux, lagoon emissions for North Carolina were estimated to be 18,175 kg yr^{-1} for H_2S, 1,640 kg yr^{-1} for DMS, and 1,230 kg yr^{-1} for DMDS. Using the RSCs overall average normalized emissions as an emission factor, and USDA production data, the total North Carolina barn emissions were calculated. H_2S emissions for North Carolina swine barns were 1.44 million kg yr^{-1}. North Carolina DMS and DMDS emissions were considerably lower, 7,870 kg yr^{-1}, and 16,176 kg yr^{-1}, respectively. By combining the emissions from the lagoon and barn, it is estimated that total H_2S emissions from swine farms in North Carolina were 1.46 million kg yr^{-1}. It is

estimated that swine farms are responsible for approximately 21% of North Carolina total H_2S emissions.

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Table 3.1. Time and frequency of canister sampling.

	Season	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Total number of samples
Lagoon	Summer	17:40	15:23	15:20	10:51	15:07	13:41	10:58	10
							13:52	11:07	
								11:16	
	Fall	16:30	14:01	16:25	15:33	15:24			10
				16:42	16:01	15:34			
						15:43			
						16:00			
	Winter	16:28	14:25	15:45	10:31				11
		16:41	14:36	16:01	10:42				
		16:50		16:32	10:52				
	Spring	12:36	11:50	15:08	12:37				10
		12:45	11:59	15:17	12:48				
		12:57	12:08						
Barn	Summer	12:24	14:40	14:12	8:36				10
			14:49	14:21	8:50				
			14:59		8:59				
			15:08						
	Fall	15:35	14:02	15:30	15:23				10
			14:19	16:01	15:34				
				16:15	15:44				
				16:25					
	Winter	14:32	12:56	13:43	12:58				9
		14:43	13:09	14:03	13:07				
				14:30					
	Spring	14:33	12:09	13:16	15:10	11:53			9
		14:45		13:25	15:21	12:01			

Table 3.2. Seasonal DMS and DMDS fluxes and corresponding environmental parameters.

Season	Flux ($\mu g\ m^{-2}\ min^{-1}$)		Lagoon Temperature (^oC)	Lagoon pH	Wind Speed (ms^{-1})	Air Temperature (^oC)	Sulfide ($mg\ L^{-1}$)
	DMS	DMDS					
Summer	0.26[a]	0.22	27.0	7.33	2.23	26.7	1.83[d]
	(0.08)[b]	(0.04)	(3.34)	(0.16)	(0.87)	(3.32)	(1.68)
	n = 10[c]	n = 8	n = 10	n = 5	n = 10	n = 10	n = 12 (8)[e]
Fall	0.11	0.04	23.3	7.63	3.07	25.5	1.48
	(0.08)	(0.01)	(1.67)	(0.16)	(2.03)	(3.01)	(1.09)
	n = 10	n = 10	n = 10	n = 10	n = 10	n = 10	n= 12 (9)
Winter	0.05	0.02	12.3	8.08	2.38	8.59	1.56
	(0.04)	(0.02)	(2.50)	(0.11)	(0.77)	(1.23)	(1.04)
	n = 11	n = 11	n = 11	n= 11	n= 11	n = 11	n= 12 (6)
Spring	0.06	0.11	19.6	8.03	4.37	18.3	1.19
	(0.03)	(0.03)	(1.77)	(0.07)	(1.80)	(6.24)	(0.28)
	n = 10	n = 10	n = 10	n = 10	n = 10	n = 10	n = 10 (7)

[a] Mean value
[b] ±1 standard deviation
[c] n is the number of canister samples
[d] represents the maximum possible average sulfide concentration, assuming that the sulfide concentrations below the detection limit are equal to 1 $mg\ L^{-1}$
[e] number of anaerobic lagoon samples collected, number in parentheses represent the number of samples at detection limit of 1 $mg\ L^{-1}$

Table 3.3. Seasonal H_2S fluxes and corresponding environmental parameters.

Season	Flux ($\mu g\ m^{-2}\ min^{-1}$)	Lagoon Temperature (^oC)	Lagoon pH	Wind Speed (ms^{-1})	Air Temperature (^oC)	Sulfide ($mg\ L^{-1}$)
Summer	3.81[a]	25.9	7.26	1.38	21.91	1.83[d]
	(3.24)[b]	(2.74)	(0.12)	(1.05)	(4.90)	(1.68)
	N = 705[c]	N = 676	N=520	N = 705	N = 705	n = 12 (8)[e]
Fall	1.17	20.5	7.52	1.68	17.81	1.48
	(1.62)	(2.91)	(0.10)	(1.69)	(6.43)	(1.09)
	N = 646	N= 645	N = 559	N=646	N= 646	n= 12 (9)
Winter	0.08	12.2	8.02	2.05	6.97	1.56
	(0.09)	(2.14)	(0.14)	(1.19)	(5.73)	(1.04)
	N = 631	N= 605	N = 631	N = 631	N= 631	n= 12 (6)
Spring	0.27	19.9	8.03	2.76	14.45	1.19
	(1.71)	(2.09)	(0.10)	(1.74)	(6.81)	(0.28)
	N = 478	N = 478	N = 469	N = 469	N= 469	n = 10 (7)

[a] Mean value

[b] ±1 standard deviation

[c] N represents the number of 15 minute averaged data points

[d] represents the maximum possible average sulfide concentration, assuming that the sulfide concentrations below the detection limit are equal to 1 $mg\ L^{-1}$

[e] number of anaerobic lagoon samples collected, number in parentheses represent the number of samples at detection limit of 1 $mg\ L^{-1}$

Table 3.4. r^2 values and corresponding p-values for the relationship between DMS and DMDS flux and environmental parameters.

	pH	Lagoon Temperature	Air Temperature
DMS	0.49	0.46	0.35
	p<0.0001	p<0.0001	p<0.0001
DMDS	0.24	0.39	0.25
	p = 0.0031	p<0.0001	p=0.0012

Table 3.5. RSCs lagoon emissions.

	Season	Flux ($\mu g\ m^{-2}\ min^{-1}$)	Lagoon Surface Area (m^2)	Emissions ($g\ day^{-1}$)
H_2S	Summer	3.81	17702	97.1
	Fall	1.17	17702	29.8
	Winter	0.08	18372	2.12
	Spring	0.27	18802	7.31
Overall average				**34.1**
DMS	Summer	0.26	17702	6.63
	Fall	0.11	17702	2.80
	Winter	0.05	18372	1.32
	Spring	0.06	18802	1.62
Overall average				**3.09**
DMDS	Summer	0.22	17702	5.61
	Fall	0.04	17702	1.02
	Winter	0.02	18372	0.53
	Spring	0.11	18802	2.98
Overall average				**2.54**

Table 3.6. Seasonal concentrations, ventilation rates, emissions and corresponding environmental parameters for DMS and DMDS.

Season	Concentration (ppb)		Ventilation rate (m^3 min^{-1})	Emissions (g day^{-1})		Barn Temperature (^oC)	Ambient Temperature (^oC)
	DMS	DMDS		DMS	DMDS		
Summer	0.18[a]	0.47	2040	0.90	4.25	30.27	31.15
	(0.22)[b]	(0.39)	(589)	(0.90)	(2.38)	(3.18)	(2.48)
	n[c] = 10	n = 10	n =10	n = 10	n = 10	n = 10	n = 10
Fall	0.89	1.02	725	2.19	4.19	16.42	23.70
	(0.61)	(0.34)	(289)	(1.28)	(2.03)	(3.67)	(1.81)
	n = 10	n = 10	n = 10	n = 10	n = 10	n = 10	n = 10
Winter	0.84	0.66	435	1.10	1.41	14.05	19.78
	(0.41)	(0.32)	(296)	(0.50)	(0.98)	(4.15)	(2.78)
	n = 9	n = 9	n = 9	n =9	n = 9	n = 9	n = 9
Spring	0.57	0.50	850	1.56	1.90	22.42	27.61
	(0.25)	(0.51)	(366)	(0.51)	(1.31)	(3.47)	(1.62)
	n = 9	n = 9	n = 9	n = 9	n = 9	n = 9	n = 9

[a] Mean value

[b] ±1 standard deviation

[c] n is the number of canister samples

Table 3.7. Seasonal concentrations, ventilation rates, emissions and corresponding environmental parameters for H_2S.

Season	Concentration (ppb)	Ventilation rate (m^3 min^{-1})	Emissions (g day^{-1})	Barn Temperature (^oC)	Ambient temperature (^oC)
Summer	72[a] , 73[b]	1763	189	27.9	26.0
	(43)[c]	(691)	(42.4)	(2.7)	(4.1)
	N[d] = 518	N = 518	N = 518	N = 518	N = 518
Fall	327, 307	327	206	19.9	8.4
	(158)	(180)	(88.7)	(2.4)	(5.2)
	N = 741	N = 741	N = 741	N =740	N = 741
Winter	164, 150	262	79.8	18.4	11.3
	(63)	(174)	(53.6)	(3.8)	(6.2)
	N = 507	N = 507	N = 507	N = 507	N = 507
Spring	631[e], 645	601	647[f]	26.5	19.0
	(240)	(321)	(219)	(1.5)	(4.2)
	N = 649	N = 649	N = 649	N =630	N =632

[a] Mean value
[b] Average daily mean value
[c] ±1 standard deviation
[d] N represents the number of 15 minute averaged data points
[e] 27% of the 15 minute averaged data points, had at least one minute average above the limit of detection of the analyzer

Table 3.8. Concentration of RSCs from swine CAFOs.

Reference	Location	Vent system	Manure collection system/description of sample location	Facility type	Month	Concentration (ppb) DMS	DMDS
Clanton and Schmidt, (2000)	MN	M	Deep pit/room air	Grow/Finish	Apr	2.2	3.9
Clanton and Schmidt, (2000)	MN	M	Deep pit/room air	Grow/Finish	Apr	5.1	1.2
Clanton and Schmidt, (2000)	MN	M	Deep pit/pit fan	Gestation	Apr	2.2	ND
Clanton and Schmidt, (2000)	MN	M	Pull plug/wall fan	Nursery	May	ND	ND
Clanton and Schmidt, (2000)	MN	M	Pull plug/room air	Nursery	May	ND	ND
Clanton and Schmidt, (2000)	MN	M	Pull plug/pit fan	Nursery	May	ND	ND
Trabue et al., (2008)	IA	M	Pull plug/room air	Finish	NS	ND	ND
Trabue et al., (2008)	IA	M	Pull plug/room air	Farrow	NS	ND	ND
Trabue et al., (2008)	IA	N	Deep pit/pit fan	NS	NS	5.3	<LOQ
Kim et al., (2007)	S. Korea	M	Deep pit/room air near fan outlet	Gestation	Mar-May & Sep-Nov	2.1	0.9
Kim et al., (2007)	S. Korea	M	Deep pit/room air near fan outlet	Farrow	Mar-May & Sep-Nov	2.0	1.2
Kim et al., (2007)	S. Korea	M	Deep pit/room air near fan outlet	Nursery	Mar-May & Sep-Nov	2.3	1.4
Kim et al., (2007)	S. Korea	M	Deep pit/room air near fan outlet	Grow	Mar-May & Sep-Nov	6.0	3.4
Kim et al., (2007)	S. Korea	M	Deep pit/room air near fan outlet	Finish	Mar-May & Sep-Nov	8.4	4.7
Blunden et al., (2008)[a]	NC	M	Shallow pit/ outside of barn near fan	Finish	Oct	0.2	0.1
Blunden et al., (2006)[a]	NC	M	Shallow pit/ outside of barn near fan	Finish	Feb	0.1	0.2
Blunden et al., (2006)	NC	N	Shallow pit/ outside of barn near fan	Finish	Sep	1.6	0.2
Blunden et al., (2006)	NC	N	Shallow pit/ outside of barn near fan	Finish	Jan	ND	ND
This study	NC	M	Shallow pit/at fan outlet	Finish	Jun	0.2	0.5
This study	NC	M	Shallow pit/at fan outlet	Finish	Nov	0.9	1.0
This study	NC	M	Shallow pit/at fan outlet	Finish	Feb	0.8	0.6
This study	NC	M	Shallow pit/at fan outlet	Finish	Apr	0.6	0.5

ND = No detection, NS = Not specified, <LOQ below limit of quantification.
[a] Measurements made at same swine CAFO.

Table 3.9. Barn pig production numbers and the calculated normalized emission factor for the RSCs.

Sampling Season	Number of Pigs	Number of weeks in rotation	Average Weight (kg)	Total Live Animal Weight (kg)	Normalized Emissions (g day^{-1} AU^{-1}) H_2S	DMS	DMDS
Summer	884.5	7-8	48.7	43,049	2.20 (0.49)[a]	0.010 (0.01)	0.050 (0.03)
Fall	994.5	4-5	34.6	34,428	2.99 (1.27)	0.032 (0.02)	0.061 (0.03)
Winter[b]	476	20-21	116.6	55,513	0.72 (0.48)	0.010 (0.01)	0.013 (0.01)
Spring	874.5	8-9	50.6	44,262	7.31 (2.48)	0.018 (0.01)	0.021 (0.02)
Overall average Emissions					3.3	0.018	0.037

[a] ± 1 standard deviation

[b] Occurred at end of rotation, when some pigs had been sold.

Table 3.10. RSCs odor thresholds and characteristics.

	Odor Threshold (ppb)	**Odor Characteristic** [e]
H_2S	17.8[a] 4.5[b] 8.1[c],	Rotten eggs
DMS	2.24[a], 9.8-20[b]	Stench
DMDS	12.3[a] 0.78-3.6[d]	Putrid garlic

[a] Devos et al. (1990)
[b] American Industrial Hygiene Association (AIHA), (1989)
[c] Amoore and Hauatala, (1983)
[d] Haz-Map, (2009). Note: The reference for this odor threshold was not provided
[e] Odor characteristic from Schiffman et al. (2001)

Table 3.11. H_2S barn concentrations in comparison to their odor thresholds.

	H_2S concentration (ppb)	Number and % of 15 minute average concentrations above an order of magnitude higher than average H_2S odor threshold **101.3 ppb**
Summer	72[a] (43)[b], 15-197[c] n =518[d]	139, 27%
Fall	327 (158), 43-796 n = 741	690, 93%
Winter	164 (63), 42-345 n = 507	399, 79 %
Spring	631 (240), 15-1000[e] n = 649	631, 97%

[a] Mean value
[b] ± 1 standard deviation
[c] Range
[d] N represents the number of 15 minute average data points
[e] 27% of the 15 minute average points had concentrations above the limit of the analyzer (1000 ppb).

Table 3.12. DMS and DMDS barn concentrations in comparison to their odor threshold.

		Number of samples exceeding odor threshold			
	Odor Threshold (ppb)	Summer	Fall	Winter	Spring
DMS	2.24	0[a]	0	0	0
		0.51[b]	2.09	1.58	0.92
DMDS	0.78	3 N	8 Y	4 N	2 N
		1.17	1.53	1.08	1.69

[a] If there are individual samples exceeding the odor threshold, the letter indicates if the seasonal average exceeds the odor threshold, Y=Yes, N=No

[b] highest individual sample concentration in each season

Table 3.13. Live animal weight calculations for the state of North Carolina for the December 2008-February 2009 period (USDA, 2009).

	Average Weight (lb)	Number	Total Weight (lb)
Breeding	433	980,000	$4.243 * 10^8$
< 60 lbs	30	3,300,000	$9.900 * 10^8$
60-119 lbs	90	1,930,000	$1.737 * 10^8$
120-179 lbs	150	1,750,000	$2.625 * 10^8$
>180 lbs	220	1,640,000	$3.608 * 10^8$
Total live animal weight (lbs)			$1.320* 10^9$
Total live animal weight (kg)			$5.989* 10^8$

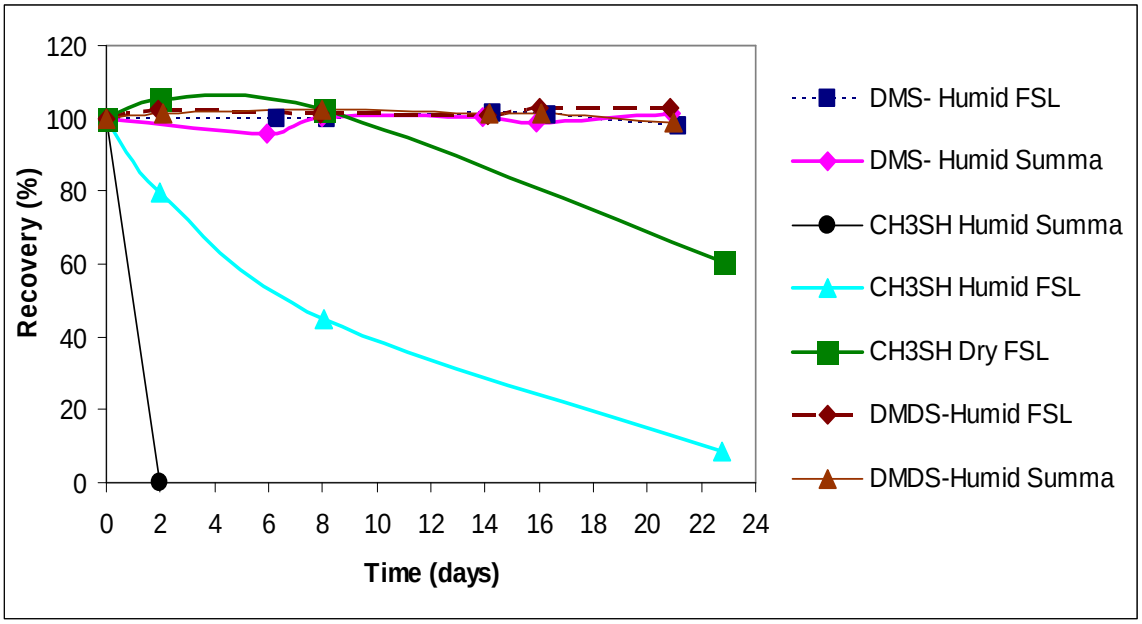


Figure 3.1. The stability of RSCs in different types of canister and varying moisture.

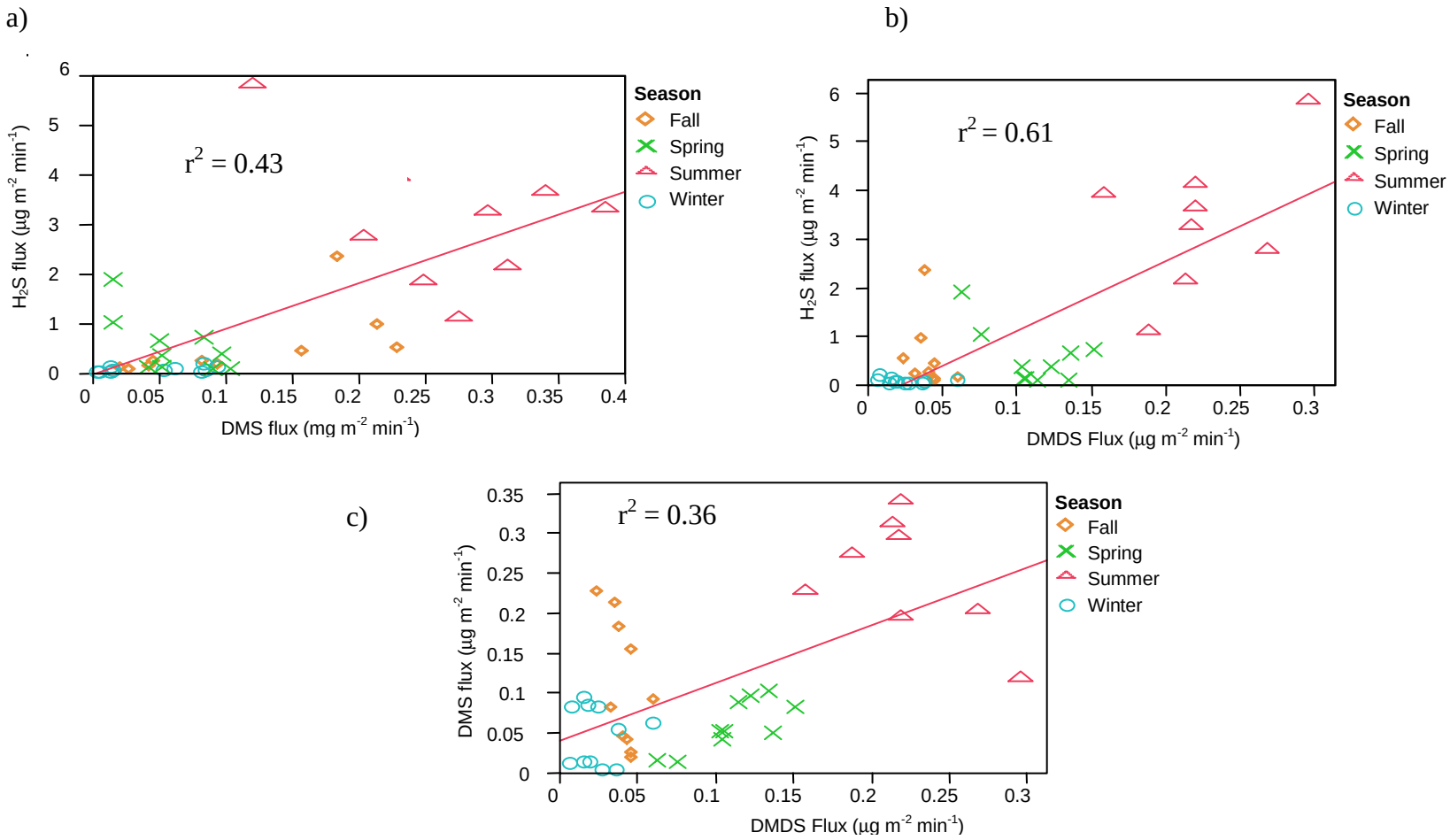
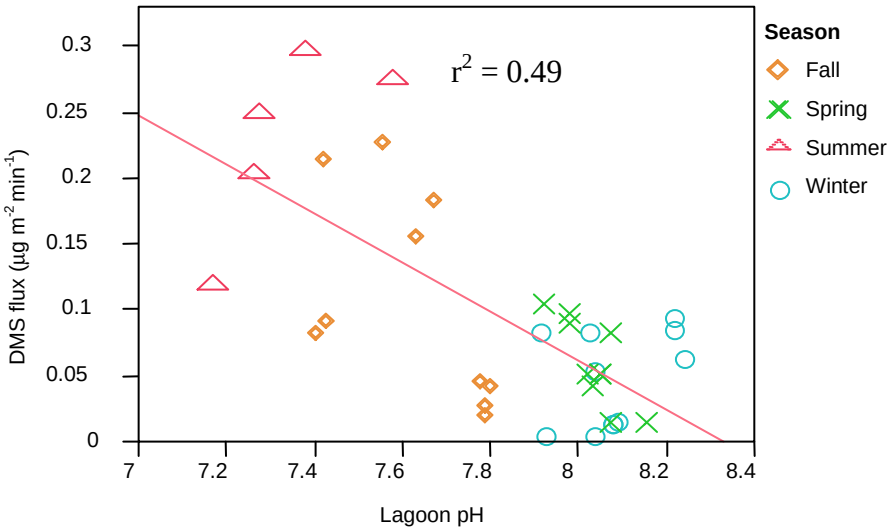


Figure 3.2. The relationships between a) H_2S flux (µg m^{-2} min^{-1}) and DMS flux (µg m^{-2} min^{-1}), b) H_2S flux (µg m^{-2} min^{-1}) and DMDS flux, c) DMS flux (µg m^{-2} min^{-1}) and DMDS flux (µg m^{-2} min^{-1}).

a)



b)

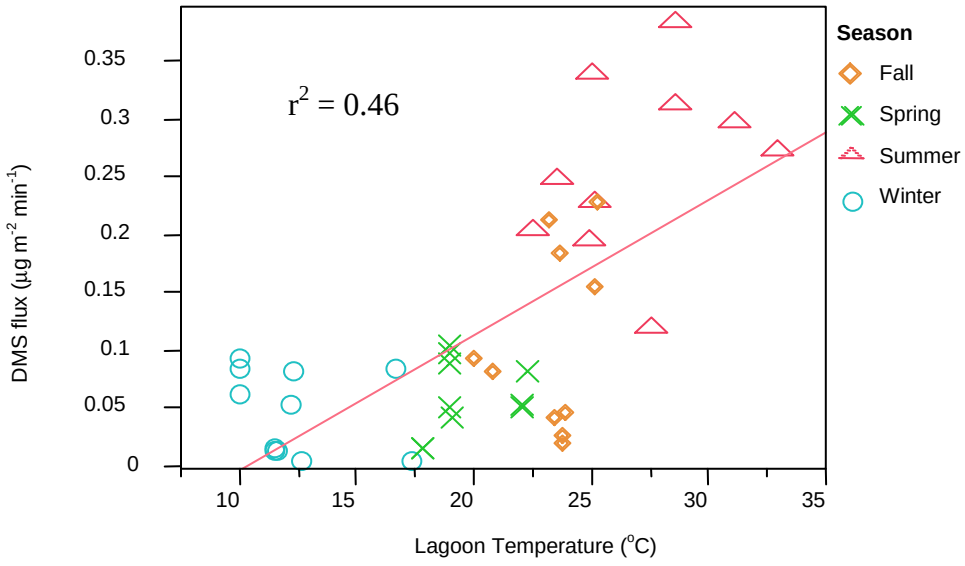
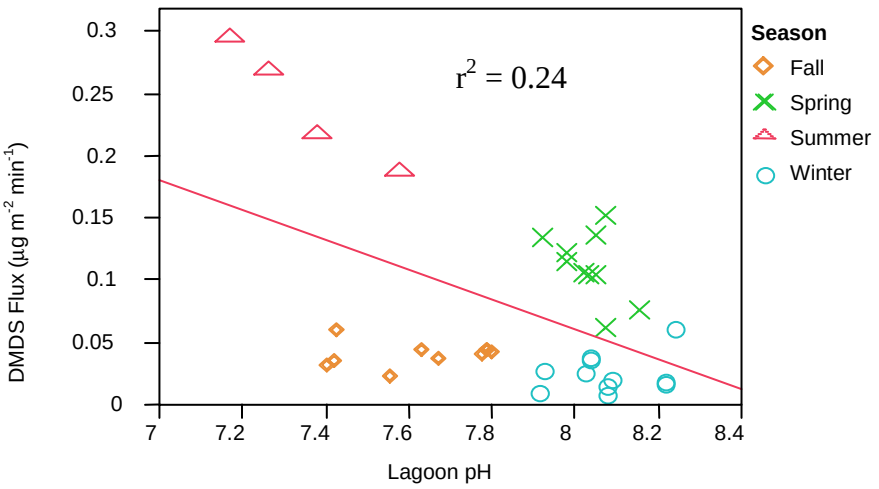


Figure 3.3. DMS flux (µg m^{-2} min^{-1}) vs. a) lagoon temperature (^{o}C) b) lagoon pH.

a)



b)

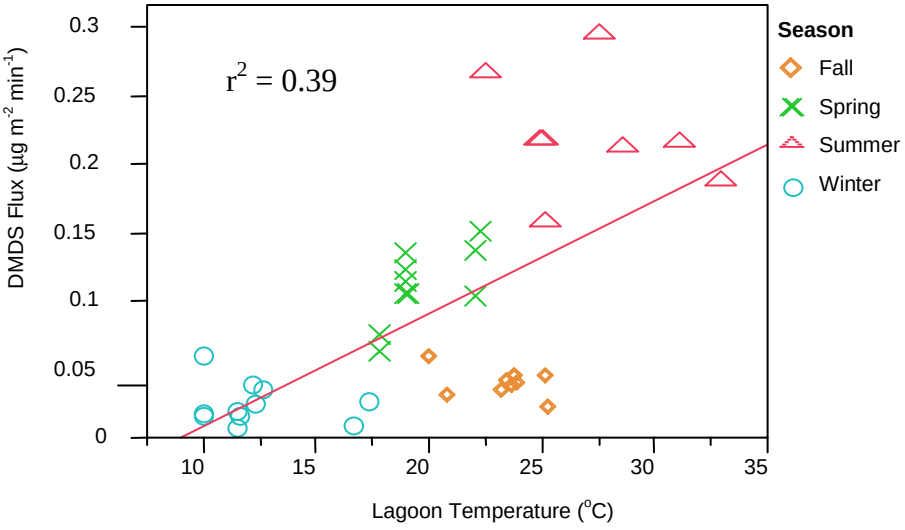


Figure 3.4. DMDS flux (µg m^{-2} min^{-1}) vs. a) lagoon temperature (^{o}C) b) lagoon pH.

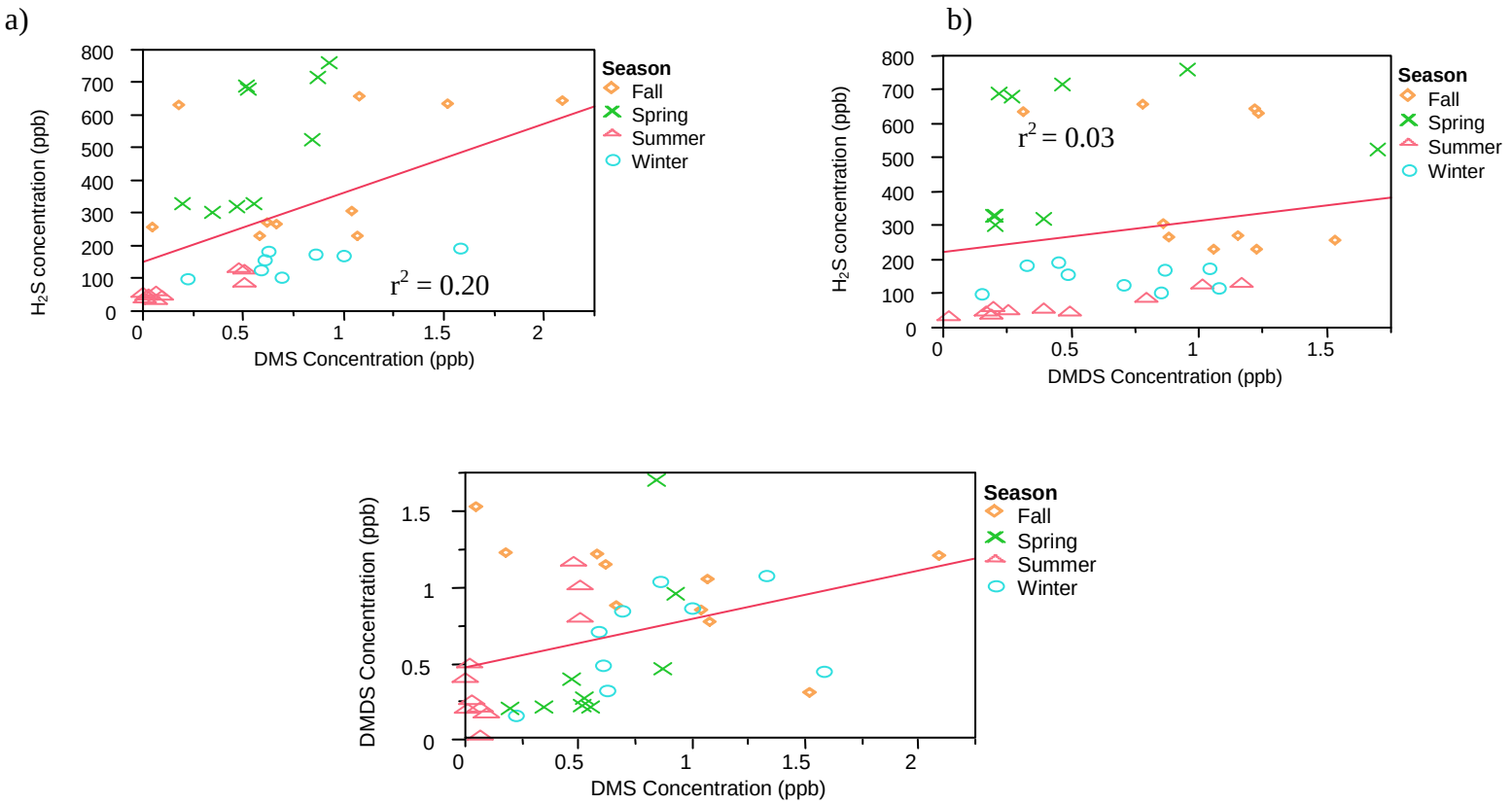


Figure 3.5. The relationships between a) H_2S concentration (ppb) and DMS concentration (ppb), b) H_2S concentration (ppb) and DMDS concentration c) DMS concentration (ppb) and DMDS concentration (ppb).

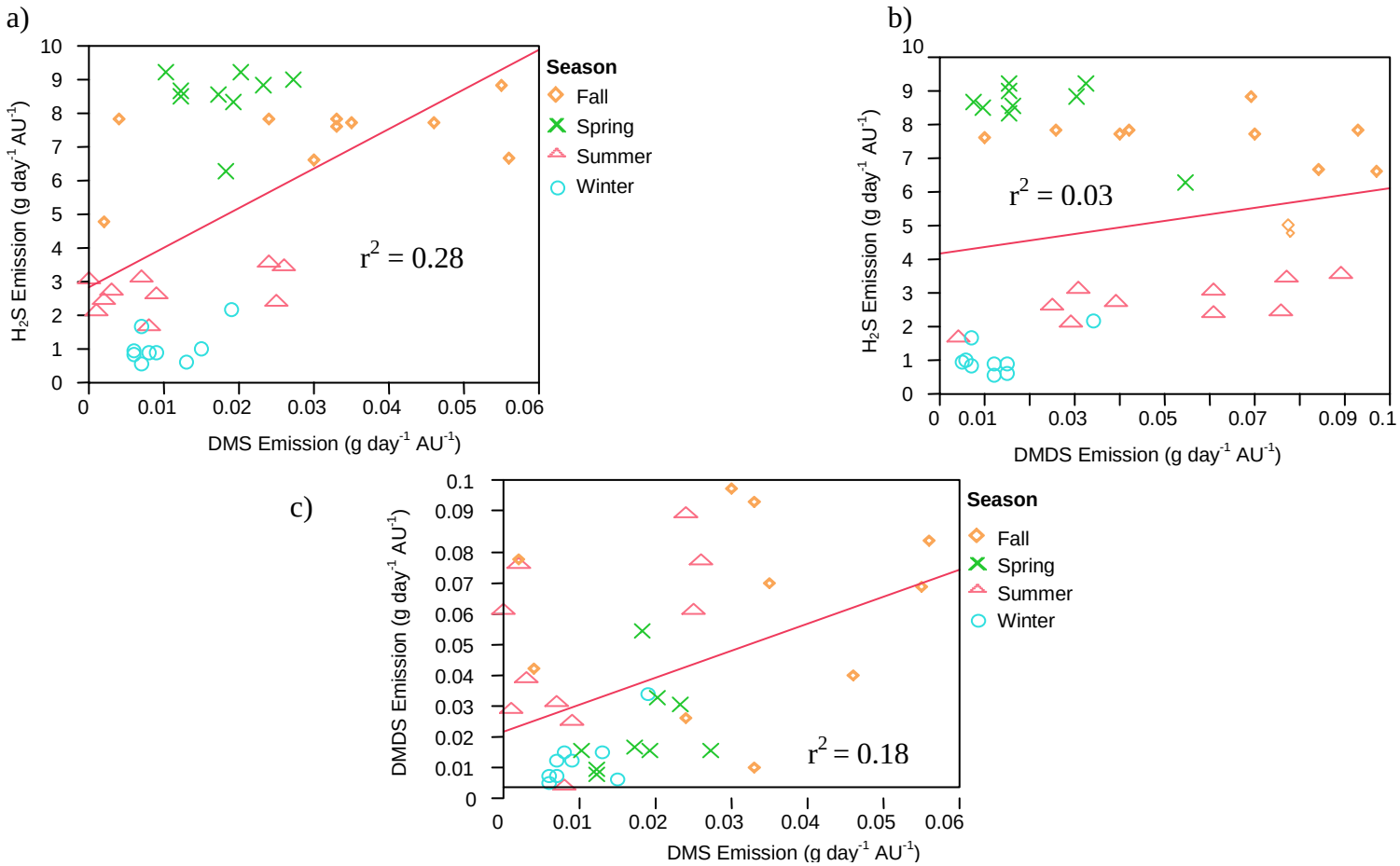
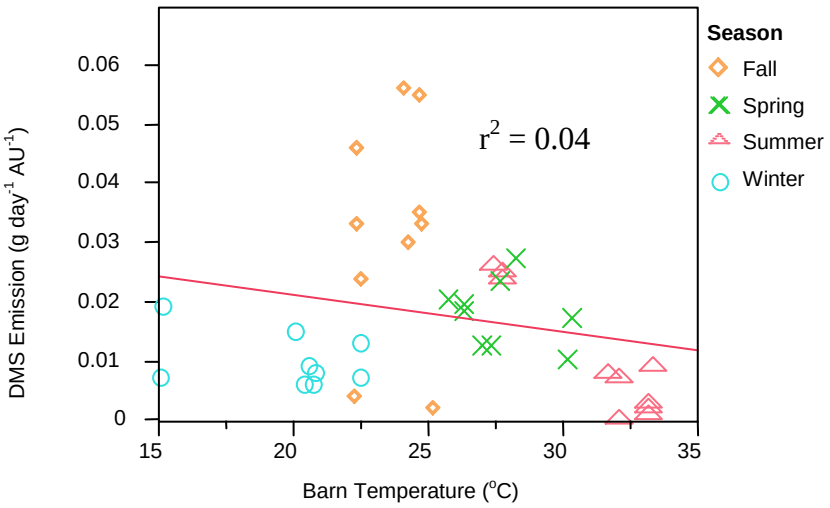


Figure 3.6. The relationships between a) H_2S emissions (g day^{-1} AU^{-1}) and DMS emissions (g day^{-1} AU^{-1}), b) H_2S emissions (g day^{-1} AU^{-1}) and DMDS emissions (g day^{-1} AU^{-1}), c) DMS emissions (g day^{-1} AU^{-1}) and DMDS emissions (g day^{-1} AU^{-1}).

a)



b)

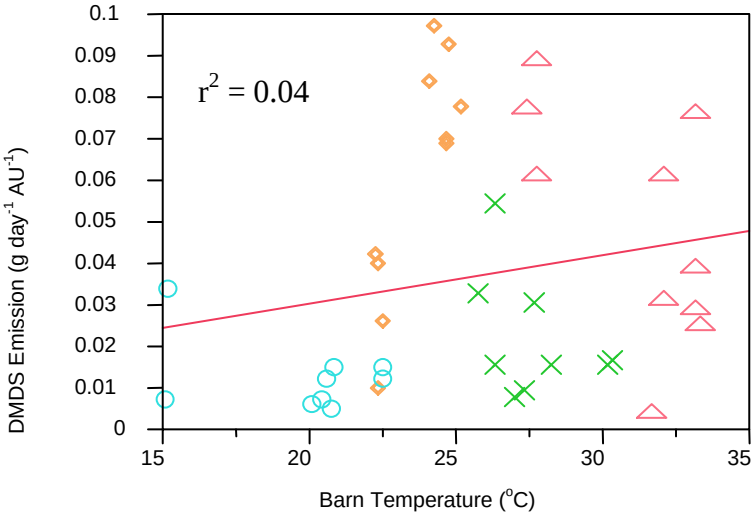


Figure 3.7. The relationship between a) barn temperature and DMS emission (g day^{-1} AU^{-1}), b) barn temperature and DMDS emission (g day^{-1} AU^{-1}).

CHAPTER IV.
Characterizing Non-Methane Volatile Organic Compounds Emissions from a Swine Concentrated Animal Feeding Operation

ABSTRACT

Emissions of non-methane volatile organic compounds (NMVOCs) were measured from a swine concentrated animal feeding operation (CAFO) in North Carolina. NMVOCs were measured using SUMMA and fused-silca lined (FSL) canisters. Measurements were made from both an anaerobic lagoon and barn in each of the four seasonal sampling periods during the period June 2007 through April 2008. In each sampling period, nine to eleven canister samples were taken from both the anaerobic lagoon and barn over a minimum of four different days during a period of ~1 week.

The canisters were analyzed using a gas chromatography flame ionization detection (GC-FID) system. Measurements of meteorological and physiochemical parameters were also made during sampling. In lagoon samples, 12 significant NMVOCs (i.e. had significantly higher fluxes in comparison to other compounds) were identified, which included three alcohols (ethanol, 2-ethyl-1-hexanol, and methanol), six aldehydes (acetaldehyde, decanal, heptanal, hexanal, nonanal and octanal), two ketones (acetone and methyl ethyl ketone), and a phenol (4-methylphenol). The overall average fluxes for these NMVOCs, ranged from 0.08 $\mu g\ m^{-2}\ min^{-1}$ for 4-methylphenol to 2.11 $\mu g\ m^{-2}\ min^{-1}$ for acetone. Seven of the twelve NMVOCs had a significant negative relationship with pH (4-methylphenol, acetaldehyde, decanal, heptanal, hexanal, octanal and 2-ethyl-1-hexanol), three a significant positive relationship with lagoon temperature (methyl ethyl

ketone, acetone and nonanal), and one a significant positive relationship with air temperature (methanol). In barn samples, there were six significant NMVOCs identified. These consisted of two alcohols (methanol and ethanol), two ketones (acetone and 2-3 butanedione), an aldehyde (acetaldehyde) and a phenol (4-methylphenol). Of the six significant NMVOCs, ethanol had the highest overall average concentration with a concentration of 16.21 ppb. 4-methylphenol had the lowest overall average concentration with a concentration of 2.87 ppb. Overall average normalized NMVOC emission rates ranged from 0.45 g day^{-1} AU^{-1} for ethanol to 0.16 g day^{-1} AU^{-1} for acetaldehyde. Eight odorous NMVOCs were identified in canister samples (2-3-butanedione, decanal, ethylbenzene, heptanal, hexanal, 4-methylphenol, nonanal, and octanal), with four of these NMVOCs (2-3-butanedione, decanal, 4-methylphenol and nonanal) exceeding their odor threshold at the barn fan exhaust. Of the significant NMVOCs identified in lagoon and barn emissions, 4 of them were hazardous air pollutants (HAPs) (acetaldehyde, methanol, 4-methylphenol and methyl ethyl ketone). A further eight HAPs were also identified in lagoon and barn samples. These were benzene, ethyl benzene, hexane, methyl chloride, styrene, xylene, toluene and 2,2,4 trimethylpentane.

Using overall average lagoon and barn emissions, the total emissions from swine CAFOs in North Carolina was estimated for the NMVOCs. Ethanol had the largest total NC emission of 206,367 kg yr^{-1}. The barns were found to have higher emissions than the lagoons for all NMVOCs except one, contributing between 72.7-100% of total NC emissions. Acetaldehyde was determined to be the NMVOC with the highest ozone forming potential.

4.1. INTRODUCTION

Concentrated agricultural feeding operations (CAFOs) emit a number of trace gases including non-methane volatile organic compounds (NMVOCs). In North Carolina, the primary CAFO is swine, with a swine population of ~ 10 million, which is mostly concentrated in the southeastern coastal plain. The emission of NMVOCs from swine CAFOs in North Carolina is of concern due to their potential environmental impacts. Certain NMVOCs are odorous. Odorous emissions are important locally, as they can potentially effect human health (Schiffman and Williams, 2005) and their quality of life (Wing and Wolf, 2000; Thu et al., 1997). Additionally, 162 of the 188 hazardous air pollutants (HAPs) are NMVOCs (U.S. EPA, 2009a). HAPs are defined by the U.S. EPA as pollutants that are known to cause cancer or other serious health effects such as damage to the immune system, reproductive, developmental, neurological, and respiratory effects (U.S. EPA, 2009b). NMVOC emissions can also have regional effects. NMVOCs are generally reactive, and can through a set of reactions form ozone. Ozone can have negative impacts on the human respiratory system, reducing lung capacity and increasing the development of illnesses such as asthma (Lippmann, 1993).

In comparison to other trace gases (i.e. ammonia, methane), measurements of NMVOC concentrations and emissions from swine CAFOs have been limited. NMVOC research studies include reports of barn concentrations (Blunden et al., 2005; Trabue et al., 2008), concentrations from a deep basin waste storage system (Zahn et al., 1997), and identification of compounds present in anaerobic lagoon water and barn air (Schiffman et

al., 2001). Currently, there is no known study that has reported NMVOC emissions from swine CAFOs with respect to seasonal and environmental variations.

This paper presents the measurement of NMVOC emissions over four seasonal sampling periods from an anaerobic lagoon and barn at a swine CAFO in North Carolina. The emissions are evaluated with respect to seasonal variations and environmental factors.

The potential environmental impacts of NMVOC emissions from swine CAFOs will be assessed in a number of ways; firstly, by comparing compounds' concentrations to their odor threshold. Additionally, the number of HAPs emitted by swine CAFOs will be identified. Measured emissions will also be used to calculate total North Carolina NMVOC emissions from swine CAFOs. These emissions' and compounds' reactivity with the hydroxyl radical (OH) will be used to assess which NMVOCs have the largest potential to form ozone.

4.2. METHOD AND MATERIALS

4.2.1. Sampling Site

The sampling site was a swine CAFO located in eastern North Carolina. The swine CAFO has eight barns, which are mechanically ventilated. The waste at the swine CAFO is dealt with, using a waste management method known as 'lagoon & spray technology'. In this method, swine waste accumulates in a shallow pit under a slatted floored barn. This waste is then flushed on a weekly basis into an anaerobic lagoon. The waste from the lagoon can then be sprayed on crops as a source of nutrients.

Additionally, the lagoon waste is used to flush the shallow pit. This waste management method is used by most swine CAFOs in North Carolina.

4.2.2. Sampling Scheme

Measurements of NMVOC emissions were made from both the anaerobic lagoon and barn. Lagoon measurements were made using a dynamic-flow through chamber system over an approximate one week period. Barn measurements were similarly made over a one week period. Concentration measurements were made by placing a sample line directly in front of a ventilation fan. To calculate the emissions, the fan ventilation rate was simultaneously measured. Measurements were made over the four seasonal periods of the year: summer, June 8th-June 28th; fall, October 20th- November 12th, 2007; winter, February 8th –February 29th, 2008; spring, April 11th –April 28th, 2008.

4.2.3. Field Sampling Technique and Instrumentation

4.*2.3.1. Stability of NMVOCs in Canisters*

Field samples were collected using both 6-litre (L) SUMMA and fused-silica lined (FSL) canisters. A wide range of NMVOCs have been found to be stable in humid SUMMA and FSL canisters. The stability of NMVOCs in humidified SUMMA was investigated by Brymer et al. (1996). Brymer et al. (1996) analyzed the stability of 194 NMVOCs in SUMMA canisters at 70% relative humidity (RH) covering a wide range of NMVOC groups including alcohols, aldehydes, alkynes, alkenes, alkanes, aromatics and ketones. NMVOC stability was examined after 7 and 30 days. Results showed that 168

out of 194 compounds were deemed stable after 30 days. Compounds were considered stable if (1) the ANOVA analysis storage variability was less than 10% of the mean concentration, (2) if the mean day 7 and day 30 concentrations are within ±1 standard deviation, or (3) the time vs. concentration slope does not have a statistically negative slope. Ochiai et al. (2002) performed a comprehensive study on the recovery and stability of 58 NMVOCs in SUMMA and FSL canisters. The NMVOCs examined included a range of chemical groups including halogenated hydrocarbons, aromatic hydrocarbons, alcohols, ketones, esters, ethers, nitriles and thiols. The compounds' stability was examined at low ppb concentrations under varying levels of humidification ((8%, 27%, 39%, 53% and 99%). After 28 days at 53% RH, which was the RH in their study which would generally portray conditions at a swine CAFO, acceptable recoveries (>80%) were found in SUMMA and FSL canisters for all compounds expect four thiols.

4.2.3.2. Field sampling

During each sampling period, 9-11 canister samples were taken from each the lagoon and barn. Before sampling, the canisters were cleaned using a XonTech Model 960 canister cleaning system. This system uses a cycle of cleaning. Canisters are evacuated, filled with humidified air, and then heated to 120^{o}C. Each canister was cleaned using two cycles. Afterwards the canisters are evacuated by the system to < 0.05 mm Hg. Both 6-L SUMMA and FSL canisters were used for sampling, of which approximately a quarter were FSL canisters. Canister samples were taken over ~ five minute periods during different times of the day (from 8:00-18:00 EST). A summary of the time and frequency of canister sampling is provided in Table 4.1. Canister samples

from the lagoon and barn were collected from a minimum of four different days over each sampling period.

4.2.3.3. Analytical System

Samples were analyzed using a Gas Chromatography-Flame Ionization Detection (GC-FID) system at the National Exposure and Research Laboratory of the U.S. Environmental Protection Agency (EPA) in Research Triangle Park, NC. The FID detects in parts per billion carbon (ppbc). Compounds were detected based on retention time. The system has a library of ~ 300 compounds retention times. To convert from ppbC to ppb, the effective carbon number for the compound is used, which is available from past literature (Scanlon and Willis, 1985; Kallai and Balla, 2002; Jorgensen et al., 1990). To confirm the accuracy of the compound identification procedure and identify unknown compounds, a gas chromatography-mass spectrometry system (GC-MS) was used.

For more information on the GC-FID and GC-MS methodologies, the reader is referred to chapter III.

4.2.4. Lagoon, Barn and Environmental Parameter Measurements

A summary of the lagoon, barn and environmental parameters measurements are presented in this paper. Further information on the measurement methodology is provided in chapters II and III.

4.2.4.1. Lagoon Measurements

Anaerobic lagoon flux measurements were made using a dynamic flow-through chamber system (Blunden and Aneja, 2008; Aneja et al., 2000). Compressed cylinder

zero air flows into the chamber through Teflon tubing at a flow rate of 4-6 L min^{-1}. It should be noted that approximately half of the cylinders used in this experiment were sampled and analyzed by the GC-FID to confirm that the cylinders contained zero air. A Teflon impeller rotates inside the chamber, ensuring that the air is well mixed similarly to ambient air. The air then leaves the chamber and flows through more Teflon tubing into the canisters. The steady state flux is thus determined by the following equation:

$$J = [C\ ]\left[\frac{q}{V}\right]h \quad (1)$$

where J, the compound flux is a function of C, the compound concentration in the carrier gas, q, the flow rate of the carrier gas, and v and h, which are the volume and height of the chamber, respectively.

4.2.4.2. *Barn Measurements*

Barn emissions were measured from one of the eight barns at the swine CAFO. The barn used five fans for ventilation, which were located on the west side of the barn facing towards the anaerobic lagoon. As temperature increases inside the barn, the fans turn on in a set sequence. The concentration was measured by placing a Teflon sampling line directly in front of the first fan to turn on. The concentration distribution was assumed uniform across the fan. Additionally, the concentration was assumed to be the same for all five fans. While collecting barn samples, background barn samples were simultaneously collected, upwind of the swine barns. Net sample concentrations were calculated for each compound.

To calculate barn emissions, the concentration was multiplied by the total fan flow rate from each of the five fans. Each individual fan flow rate was calculated using the following equation:

$$Calculated\ fan\ flow\ rate = Manufactures\ fan\ flow\ rate \times \left(\frac{Measured\ RPM}{Specified\ RPM}\right) \quad (2)$$

where RPM represents the revolutions per minute of the fan. The RPM of the fans were measured by attaching motors to the fans that produced a voltage, when the fans were turning. Additionally, manufactures flow rate was adjusted for the average static pressure difference between the inside and outside of the barn. During sampling, fan voltages were recorded and used to calculate the ventilation rate.

4.2.4.3. Environmental Parameter Measurements

During lagoon measurements, lagoon temperature and ph were recorded at a depth of ~7cm below the lagoon surface. For barn sampling, barn temperature was measured at the fan outlet. During both lagoon and barn sampling, meteorological measurements of wind speed and wind direction at a height of 10 m were made. Additionally, measurements of air temperature, relative humidity and solar radiation were made at a height of 2 m.

4.3. RESULTS AND DISCUSSION

4.3.1. Lagoon Fluxes

Observational analysis suggests that there are over 100 NMVOCs in lagoon canister samples. Of these NMVOCs, there were 12 compounds that had

significantly higher emissions in comparison to other NMVOCs, and were identified in almost every sample. Of these 12 NMVOCs, three were alcohols, (ethanol, 2-ethyl-1-hexanol, and methanol), six were aldehydes, (acetaldehyde, decanal, heptanal, hexanal, nonanal, and octanal), two were ketones, (acetone and methyl ethyl ketone), and one was a phenol, (4-methylphenol). All 12 compounds were identified by retention time, and confirmed by GC-MS. These compounds' seasonal fluxes and their overall average flux are shown in Table 4.2. It should be noted that for hexanal and heptanal, there may be possible system peak interference on some samples, therefore ten hexanal samples and one heptanal sample were excluded from analysis. Additionally, in four brand new canisters (i.e. had not been used before), there were extremely high levels of methanol, significantly above the concentrations observed in this study. It can be concluded that these high methanol concentrations were the result of the manufacture's canister cleaning process, as methanol may be used as a cleaning agent. Therefore these methanol samples were excluded from analysis. It should be noted that canister sampling was conducted during the daytime. As observed for the continuously measured H_2S lagoon flux in chapter II, there is diurnal variation in lagoon fluxes, therefore the flux values presented for the NMVOCs are not representative of a full day as they do not take into account nighttime variations in flux. Also, the sampling period(s) during the day represented a short sampling period (Table 4.1) and this should be taken into consideration when using the estimated flux values.

Acetone has the largest NMVOC lagoon flux with an overall average flux of 2.11 $\mu g\ m^{-2}\ min^{-1}$. This is almost twice the magnitude of the 2nd largest overall average flux,

which is methanol, with a flux of 1.19 μg m^{-2} min^{-1}. Acetaldehyde has the next largest overall average flux, with a flux of 0.66 μg m^{-2} min^{-1}, which is closely followed by ethanol and methyl ethyl ketone (MEK), with overall average fluxes of 0.59 and 0.56 μg m^{-2} min^{-1}, respectively. Other compounds had smaller overall average fluxes of less than 0.2 μg m^{-2} min^{-1}.

From Table 4.2, it can be observed that there are large seasonal variations in NMVOCs fluxes. For 10 out of the 12 NMVOCs, the highest fluxes are in the summer, with the exception of methanol and ethanol. Generally, the fluxes are significantly higher in summer than any of the other seasons. Of these ten compounds, six have their lowest flux in the spring, which included five of the six aldehyde compounds. The exception was nonanal, which had it's lowest seasonal flux in fall. There was little variation in flux between the fall, winter and spring seasons for the aldehydes. There was also little variation in MEK and 2-ethyl-1-hexanol fluxes in the fall, winter and spring seasons, with the lowest fluxes occurring in the winter and spring, respectively. The other two compounds with highest fluxes in the summer were 4-methylphenol and acetone. Both of these compounds showed greater seasonal variance in the fall, winter and spring seasons, particularly acetone. Both compounds have their lowest seasonal concentration in the fall.

As mentioned, methanol and ethanol were only the two compounds that did not have their highest fluxes in summer. For methanol the highest flux was in the fall (1.53 μg m^{-2} min^{-1}), which was slightly higher than the 2nd highest seasonal flux (1.39 μg m^{-2} min^{-1}), which was in the summer. The highest seasonal flux for ethanol was in the winter

(1.54 μg m^{-2} min^{-1}), which was significantly larger than the 2nd highest seasonal flux (0.55 μg m^{-2} min^{-1}), which like methanol was in the summer. The high winter ethanol flux is caused by two samples collected on the same day that have considerably higher fluxes than the other samples collected in the winter season. It is hypothesized that these two samples were collected during an ethanol high flux event. Methanol and ethanol lowest seasonal fluxes were in the winter and spring, respectively.

In comparison to previous anaerobic lagoon studies, Schiffman et al. (2001) identified 9 of these 12 compounds in lagoon water at a North Carolina swine CAFO. The three compounds that were not identified were methanol, ethanol and 4-methylphenol.

4.3.1.1. *Influence of Environmental Parameters on NMVOC Lagoon Flux*

Seasonal environmental parameters for the canister samples are presented in Table 4.3. Air temperature ranged from 8.59 ^{o}C in the winter to 26.74 ^{o}C in the summer. As expected, lagoon temperature followed the same pattern, varying from 12.33 ^{o}C in the winter to 27.00 ^{o}C in the summer. In the moderate seasons, fall lagoon temperature was slightly higher than spring with a temperature of 23.27 ^{o}C, compared to 19.59 ^{o}C in spring. Lagoon pH was lowest in the summer, with a value of 7.33. It was higher in the fall season with a value of 7.63. However, it was even higher in the winter and spring seasons with values of 8.08 and 8.03, respectively. The influence of environmental parameters was investigated using the coefficient of correlation (r^2), and their respective p-values, which are presented in Table 4.4. The environmental parameter, air temperature was included in the analysis, as the effect of the dynamic-flow through chamber system

on air temperature is small. Arkinson, (2003) using this chamber system for flux measurements determined the difference in air temperature to be 1.55 ± 2.30 ^{o}C between the inside and outside of the chamber.

Lagoon temperature and lagoon pH had the highest significant r^2 values ($p<0.05$) for 10 of the 12 compounds, with the exceptions being methanol and ethanol. For all 10 compounds, lagoon temperature had a positive relationship with lagoon flux, and pH had a negative relationship with lagoon flux. Of these 10 compounds, seven (4-methylphenol, acetaldehyde, decanal, heptanal, hexanal, octanal and 2-ethyl-1-hexanol) had a higher r^2 for pH than for lagoon temperature, with the highest occurring for hexanal with an r^2 value of 0.42 ($p=0.0002$) (Figure 4.1). Additionally for these seven compounds, lagoon temperature was also significant ($p<0.05$), with the r^2 value on average 0.12 less than the corresponding r^2 value for lagoon pH. Lagoon temperature had a higher r^2 for the other three compounds (MEK, acetone and nonanal), with a highest r^2 value of 0.33 ($p<0.0001$) for MEK (Figure 4.2). For these 3 compounds, lagoon pH was significant ($p<0.05$) for two of them, with the r^2 value on average 0.05 less than the corresponding r^2 value for lagoon temperature. As mentioned, methanol and ethanol did not have their highest significant r^2 values with lagoon temperature or lagoon pH. Methanol highest significant r^2 value was with air temperature ($r^2 = 0.29$, $p=0.0005$). Lagoon temperature was also significant but with a lower r^2 value ($r^2 = 0.15$, $p=0.02$). Lagoon pH though was not significant. It should be noted that there were four compounds (acetone, hexanal, MEK and methanol) that had a significant ($p<0.05$) correlation with air temperature. However, only for methanol was the air temperature r^2 value higher than the lagoon temperature r^2

value. It is not known why air temperature had a better correlation with flux than lagoon temperature. Ethanol was not found to have a significant correlation with any environmental parameters. This poor correlation is the result of the winter high flux event, which was described in the previous section. Wind speed did not have a significant correlation with any of the NMVOCs.

The positive relationship between lagoon temperature and flux, can be explained by the effect of temperature on flux, as increases in lagoon temperature can increase the mass transfer coefficient of chemical compounds at the air-lagoon surface interface. Increases in lagoon temperature can also increase the Henry's law constant which relates the equilibrium of a chemical compound at the lagoon-air surface interface. Additionally, an increase in temperature can increase the rate of decomposition and thus increase the amount of organic carbon available.

As mentioned, the relationship between lagoon flux and pH was negative i.e. as pH increased, the flux decreased. However, there is no known literature on the ionization of NMVOCs to support this analysis.

4.3.2. Barn Concentrations and Emissions

Observational analysis of barn samples showed a similar number of compounds to lagoon samples (i.e. over 100). In barn samples, six NMVOCs had significantly higher concentrations and emissions in comparison to other NMVOCs. These six compounds were also identified in almost every sample. These six compounds consisted of two alcohols (methanol and ethanol), two ketones (acetone and 2-3 butanedione), an aldehyde

(acetaldehyde), and a phenol (4-methylphenol). These compounds were all identified by retention time and confirmed by GC-MS, except for 2-3 butanedione. 2-3 butanedione was not in the retention time database, however it was identified by GC-MS. Of the six compounds, all except 2-3 butanedione was identified as a significant compound in lagoon emissions. It should be noted that 2-3 butanedione was identified in lagoon samples, however it's fluxes were < 0.01 $\mu g\ m^{-2}\ min^{-1}$, and were therefore considered negligible. Similarly to lagoon samples, there was one brand new canister in barn samples that had elevated levels of methanol, which as mentioned was attributed to the manufacture's cleaning process. This sample was excluded from further analysis.

As discussed for lagoon samples, canister samples were collected during the daytime, and are therefore not representative of a full day. Accordingly, the NMVOC barn concentrations and emissions presented do not take into account nighttime variations in emissions, which were observed for H_2S barn concentrations and emissions in chapter II. Additionally, the sampling period(s) during the day represented a short sampling period (Table 4.1) and this should be taken into account when using the estimated concentration and emission values.

Seasonal and overall average concentrations of the six significant barn compounds are presented in Table 4.5. Overall average concentrations range from 2.87 ppb for 4-methylphenol to 16.12 ppb for ethanol.

Variations can be observed in the NMVOCs seasonal concentrations (Table 4.5). Ethanol has it's highest seasonal concentration in the spring season with a concentration of 28.80 ppb and it's lowest concentration in the winter with a concentration of 8.67 ppb.

Methanol has it's highest concentration in the fall with a concentration of 20.33 ppb. In the fall season, this is the highest compound concentration. The lowest methanol concentration occurs in the summer (6.84 ppb). Acetone has it's highest seasonal concentration in spring with a concentration of 12.85 ppb and it's lowest seasonal concentration in the summer with a value of 2.03 ppb. Similarly to methanol, acetaldehyde has it's highest concentration in the fall (7.20 ppb) and it's lowest in the summer (1.44 ppb). 2-3 butanedione also has it's highest concentration in the fall with a value of 6.23 ppb. The lowest seasonal concentration occurs in the winter with a concentration of 1.36 ppb. The highest 4-methylphenol concentration occurs in the spring (5.25 ppb), and the lowest in the summer (0.95 ppb). Overall, it can be observed that all the highest seasonal concentrations occur in the spring or fall, and all the lowest in the summer or winter.

Table 4.6 presents concentrations of these six NMVOCs from previous swine CAFO barn studies. Blunden et al. (2005) made sample measurements in front of swine barns at two swine CAFOs in North Carolina. The measurements were conducted in two different seasons. One swine CAFO employed a naturally ventilated system, the other was the same sampling site as this study and therefore employed a mechanically ventilated system.

The Blunden et al. (2005) study reported concentrations of ethanol, methanol, acetaldehyde, acetone, and 4-methylphenol. In the naturally ventilated system, seasonal ethanol concentrations varied greatly. In the fall a concentration of 45.1 ppb was reported, which is higher than any of the seasonal averages reported in this study.

However, the winter concentration was 0.5 ppb, which was lower than any of the seasonal averages reported in this study. At the same sampling site, ethanol concentrations were 12.5 ppb in the winter and 1.0 ppb in the fall. Both concentrations are lower than the seasonal average concentrations reported in this study. Methanol concentrations at the naturally ventilated CAFO were 21.6 ppb in the fall, which was slightly larger than the highest seasonal concentration in this study (20.33 ppb). In the winter season a concentration of 1.2 ppb was reported, which is lower than any seasonal concentration in this study. At the same sampling site, concentrations were 3 ppb in the fall and 9ppb in the winter, which are lower than the corresponding seasonal concentrations reported in this study. Acetone concentrations (1.5 ppb and 1.7 ppb) at the same sampling site were lower than any of the seasonal averages in this study. A low acetone concentration was also measured at the naturally ventilated CAFO in winter (0.1 ppb). However, the fall concentration was of similar magnitude to concentrations in this study with a value of 13.7 ppb. Seasonal acetaldehyde concentrations were 1.8 ppb (winter) and 3.6 ppb (fall) at the naturally ventilated CAFO and 1.2 ppb (winter) and 2.1 ppb (fall) at the same sampling site. These values compare fairly well, however the concentrations are all lower than two out of the four seasonal averages (6.54 ppb and 7.20 ppb) in this study. 4-methylphenol was only identified in one of the two seasons at each sampling site. The concentration was higher for the naturally ventilated barn, 5.0 ppb compared to 1.6 ppb. These concentrations are of a similar magnitude to the seasonal concentrations reported in this study.

Schiffman et al. (2001) identified all six significant NMVOCs in barn air samples from a swine CAFO. Concentrations were reported for acetaldehyde, acetone and 4-methylphenol. However, the study did not quantify methanol, ethanol and 2-3 butanedione concentrations. Acetaldehyde was reported to have a concentration of 4 ppb, which is of similar magnitude to the concentrations reported in this study. The acetone concentration was lower than all of the seasonal concentrations in this study, with a concentration of 1 ppb. Conversely, the 4-methylphenol concentration was slightly higher than any of the seasonal concentrations in this study, with a concentration of 9 ppb.

Trabue et al. (2008) also reported the concentration of 4-methylphenol from inside a swine barn in Iowa. 4-methylphenol was identified to have a concentration of 2.4 ppb, which was within the range of seasonal concentrations measured in this study.

Overall, it can be concluded that seasonal acetone concentrations are generally higher in comparison to previous swine CAFO studies. Methanol, ethanol, acetaldehyde and 4-methylphenol seasonal concentrations however, are generally of a similar magnitude to previous studies. There have been no previous studies reporting 2-3 butanedione concentrations, although Schiffman et al. (2001) did identify the compound as being present in barn air samples.

Seasonal emissions were calculated using the ventilation rate at the time of sampling. The barn ventilation rates and the corresponding environmental parameters are presented in Table 4.7. The seasonal and overall average emissions for the six significant NMVOCs are presented in Table 4.8 in units of g day^{-1}. The NMVOC with the highest overall average emission is ethanol with a value of 37.95 g day^{-1}. Methanol has the 2nd

highest overall average emission rate with an emission of 22.24 g day^{-1}, which is only slightly higher than the overall average emission rate for acetone (19.62 g day^{-1}). The overall average emission rates of 2-3 butanedione, and 4-methylphenol are lower with similar emissions of 14.89 and 13.40 g day^{-1}, respectively. The lowest overall average emission rate is acetaldehyde with an emission of 7.97 g day^{-1}.

Four of the six compounds have their highest emission rate in the spring. These are acetone (34.85 g day^{-1}), methanol (28.46 g day^{-1}), 4-methylphenol (28.22 g day^{-1}) and ethanol, which has the highest overall seasonal emission rate with an emission of 61.34 g day^{-1}. The two other compounds, acetaldehyde and 2-3 butanedione had their highest emissions in the fall, with emissions of 13.92 g day^{-1} and 22.93 g day^{-1}, respectively. The spring and fall seasons have the 1^{st} and 2^{nd} highest seasonal emission rates for all of the six compounds apart from ethanol, where the summer season had the 2^{nd} highest seasonal flux. For all six compounds, the winter season had the lowest emission rate.

Animal weight is considered to be a factor that influences barn emissions, therefore seasonal emissions were normalized for 500 kg of live animal weight, also referred to as 1 animal unit (AU). The live animal weight, the corresponding pig production numbers and the normalized NMVOC seasonal emissions are presented in Table 4.9. Normalizing the emissions for live animal weight only affected the seasonal trend of one of the six compounds, which was methanol. As mentioned, the highest seasonal methanol emission rate was in the spring (28.46 g day^{-1}), followed by the fall with an emission rate of 26.92 g day^{-1}. However, the larger live animal weight in the spring compared to the fall, resulted in higher normalized emissions in the fall season

than the spring, 0.39 compared to 0.32 g day^{-1} AU^{-1}, respectively. The highest overall average normalized emission rate was ethanol with a value of 0.45 g day^{-1} AU^{-1}, followed by methanol and acetone with normalized emissions of 0.27 and 0.24 g day^{-1} AU^{-1}, respectively. 2-3 butanedione had a normalized emission rate of 0.19 g day^{-1} AU^{-1}, which was slightly higher than the normalized emission rate of 4-methylphenol, which was 0.16 g day^{-1} AU^{-1}. The lowest normalized emission rate of the six compounds was acetaldehyde with an emission of 0.10 g day^{-1} AU^{-1}.

There are seven compounds (decanal, 2-ethyl-1-hexanol, heptanal, hexanal, MEK, nonanal, and octanal) that were identified as significant compounds in lagoon emissions that were not significant compounds in barn emissions. These compounds, seasonal concentrations, emissions and normalized emissions are presented in Table 4.10. Emissions were normalized for 500 kg of live animal weight, using the same live animal weight data presented in Table 4.9. It should be noted that MEK concentrations were less than 0.1 ppb, therefore they were considered negligible and were not quantified. It can be observed that the concentrations and emissions of these compounds are considerably lower, and are up to two orders of magnitude lower than the six significant compounds identified in this study. It should be noted that similarly to the lagoon samples, that some hexanal, heptanal and octanal samples may have been affected by a possible system peak. Therefore three heptanal, two hexanal and one octanal sample were excluded from analysis. These seven compounds were all identified by Schiffman et al. (2001) in air samples taken from a barn at North Carolina swine CAFO.

4.3.2.1. Factors Influencing Barn Emissions

The variance in NMVOC emissions is the result of the influence of a range of factors. Some of the most important factors are those that influence the amount of organic carbon in the barn, which is determined by the amount of manure in the barn and the organic carbon content of the manure. The amount of barn manure is influenced by the total animal weight, which was taken into account in this study. However, there are other manure management factors such as the amount of time since the barn was cleaned and flushing frequency that will also influence the amount of manure inside the barn. The organic carbon content of the manure is influenced by the carbon content of the feed and the efficiency of the swine in retaining the carbon. NMVOC emissions are also influenced by environmental factors that affect the rate of release of compounds from the manure into the air. Important environmental factors that may influence emissions include temperature, which was measured at the barn fan outlet. Barn temperatures were highest in the summer, with a seasonal sample average of 31.15 ^{o}C, followed by spring and fall with seasonal sample averages of 27.43 ^{o}C and 23.81 ^{o}C, respectively. The lowest seasonal sample average was winter with a value of 20.01 ^{o}C. The influence of barn temperature on normalized emissions in this study was determined using r^2 values. Normalized ethanol emissions was found to have a weak positive relationship with barn temperature ($r^2 = 0.23$, $p<0.0022$), (Figure 4.3.). The other five significant compounds' normalized emissions were found to have little or no relationship with barn temperature, with all the r^2 values for this relationship less than 0.05 and the corresponding p-values greater than 0.05. However, the weak relationships between barn temperature and

NMVOCs normalized emissions were expected. As discussed in chapter II, the balance between the input and outputs of emissions in the barn makes it hard to determine the influence of environmental parameters.

There are other environmental factors that may influence NMVOC barn emissions such as manure pH and the air velocity above the manure surface. It was though beyond the scope of this study to measure these environmental parameters.

4.3.3. Potential Environmental Impacts

4.*3.3.1. Odor*

The emission of odorous compounds from swine CAFOs can have a health impact on people who live in the surrounding area. Chemical compounds become odorous when they exceed their odor detection threshold. This is defined as the lowest concentration of a chemical compound that produces a sensory response in the olfactory receptors of humans (American Industrial Hygiene Association, (AIHA), 1989). In odor testing, it is defined as the minimum concentration of sensory response detected in 50% of the odor panel (AIHA, 1989). Unpleasant odors cause a reaction in the human nervous system to warn us against unsafe air and food. This in turn effects the functionality of the human brain and body, which can result in the development of health symptoms and furthermore health effects (Schiffman and Williams, 2005). Chemical compounds have the potential to be odorous if they have low odor thresholds. In this study, eight odorous NMVOCs (heptanal, octanal, nonanal, decanal, ethylbenzene, 2-3 butanedione, 4-methylphenol and hexanal) were identified in barn samples from the swine CAFO. Of the eight odorous

NMVOCs, two (4-methylphenol and 2-3 butanedione) were significant NMVOCs in barn samples. Compounds were defined as odorous, if they had an odor threshold less than 10 ppb. The odor thresholds for these compounds and their odor characteristic are presented in Table 4.11. It can be observed that there the odor thresholds vary slightly. This is due to the different methodologies and sources used to determine the odor threshold.
A comparison of NMVOC barn concentrations to their odor threshold is presented in Table 4.12. Ethyl benzene concentrations were less than 0.1 ppb, therefore this compounds' concentration was considered negligible and was not included in the analysis.

4-methylphenol was the NMVOC that exceeded it's odor threshold the most frequently. Three out of the four 4-methylphenol seasonal averages were above all the odor thresholds, with a highest seasonal average of 5.25 ppb in the spring, which is ~3 ppb above the highest odor threshold, and almost two orders of magnitude higher than the lowest odor threshold. The summer seasonal average was the exception with a concentration of 0.95 ppb, which was above two of the three odor thresholds. 34 of the 38 (~89%) 4-methylphenol sample concentrations were found to exceed the lowest odor threshold of 0.068 ppb and over two-thirds (26) of the sample concentrations also exceeded the 2nd highest odor threshold of 0.264 ppb. Furthermore, exactly half of the sample concentrations (19) exceeded the highest odor threshold of 1.86 ppb. Sample concentrations were generally highest in the spring sampling season, with all nine sample concentrations exceeding the highest odor threshold in this season. However, the highest individual sample concentration was 11.67 ppb, which occurred in the winter season.

2-3 butanedione concentrations exceeded their odor threshold the second most frequently of the NMVOCs. Three of the four average seasonal concentrations were above the lowest odor threshold of 1.42 ppb, with one seasonal concentration exceeding the 2nd highest odor threshold of 4.37 ppb. No seasonal concentrations exceeded the highest odor threshold of 7.39 ppb, with the highest seasonal concentration occurring in the fall with a concentration of 6.92 ppb. 23 of the 38 (~61%) 2-3 butanedione sample concentrations exceeded the lowest odor threshold of 1.42 ppb. There were 14 (37%) sample concentrations that exceeded the 2nd highest odor threshold of 4.37 ppb and 4 (11%) sample concentrations that exceeded the highest odor threshold of 7.39 ppb. Sample concentrations were highest in the fall and spring, with the highest sample concentration occurring in the fall with a concentration of 22.28 ppb, which is ~3 times larger than the highest odor threshold.

For nonanal, only individual samples exceeded the lowest odor threshold of 0.77 ppb. The highest seasonal concentration was in the spring with a concentration of 0.64 ppb. Six (16%) of the sample concentrations exceed the lowest odor threshold. These were all from the fall and spring sampling period, with the highest sample concentration occurring in the spring with a concentration of 1.70 ppb.

Similarly to nonanal, decanal had no seasonal concentrations exceeding it's odor threshold, which was 0.89 ppb. The highest seasonal concentration was in the fall with a concentration of 0.28 ppb. However, there was one sample concentration in the fall season that was above the odor threshold, with a concentration of 1.63 ppb.

Heptanal, hexanal, and octanal sample concentrations were all below their odor thresholds. The highest seasonal heptanal concentration was spring with a concentration of 0.34 ppb, which is an order of magnitude below it's lowest odor threshold of 4.79 ppb. The spring also had the highest heptanal sample concentration with a concentration of 0.74 ppb, which was also significantly below the lowest odor threshold. The highest seasonal hexanal concentration was spring with a concentration of 0.78 ppb. The winter season had the highest hexanal sample concentration, which was 1.50 ppb. Both the highest seasonal and sample concentration were below the lowest odor threshold of 7.0 ppb. For octanal, the highest seasonal concentration was fall with a concentration of 0.15 ppb and the highest sample concentration was 0.53 ppb, which occurred in spring. Both were below the lowest odor threshold of 1.11 ppb.

4.3.3.2. Hazardous Air Pollutants

Hazardous air pollutants (HAPs) are defined by the U.S. EPA as pollutants that are known to cause cancer or other serious health effects such as damage to the immune system, reproductive, developmental, neurological, and respiratory effects (U.S. EPA, 2009b). The U.S. EPA identified 188 hazardous air pollutants (HAPs), of which 162 are NMVOCs (U.S. EPA, 2009a). In this study, four of the significant compounds emitted from the lagoon and barn were HAPs. These were acetaldehyde, methanol, 4-methylphenol, and MEK. A further HAP identified in lagoon and barn samples by retention time and GC-MS was hexane. Seasonal hexane concentrations, emissions, and normalized emissions are presented in Table 4.13. Seasonal hexane barn concentrations ranged from 0.08-1.20 ppb, with an overall average concentration of 0.63 ppb. Emissions

ranged from 0.74 g to 3.69 g day^{-1}, with an overall average emission of 1.98 g day^{-1}. Normalized emissions ranged from 0.009-0.042 g day^{-1} AU^{-1}, with an overall average emission of 0.022 g day^{-1} AU^{-1}. Hexane lagoon samples all had fluxes less than 0.01 μg m^{-2} min^{-1}, therefore the lagoon emissions were considered negligible and were not quantified. Additionally a further seven HAPs were identified by retention time in lagoon and barn samples. These were benzene, ethyl benzene, methyl chloride, styrene, xylene, toluene and 2,2,4 trimethylpentane. All of these compounds had lagoon fluxes less than 0.01 μg m^{-2} min^{-1} and barn concentrations less than 0.1 ppb, therefore these lagoon and barn emissions were considered negligible and were not quantified. Schiffman et al., (2001) identified all the HAPs in this study apart from styrene and 2,2,4 trimethylpentane.

4.3.3.3. North Carolina NMVOCs Emissions

The potential regional environmental impact of NMVOC swine CAFO emissions can be evaluated by determining the total North Carolina swine CAFO emissions. To determine the NMVOC North Carolina lagoon emissions, the total lagoon area for North Carolina was estimated. Aneja et al. (2000) used a SPOT satellite image of North Carolina to determine that the average size of a swine lagoon was approximately 1 ha (10,000 m^2). The number of swine CAFOs in North Carolina was provided by the United States Department of Agriculture (USDA). Their most recent estimate of the number of swine CAFOs was 2,800, for the year 2007 (USDA, 2009). Using this information and the overall seasonal lagoon flux, the NMVOC North Carolina lagoon emissions were estimated.

The NMVOC North Carolina barn emissions were calculated based on the most recent estimate of the number and weight of hogs in North Carolina (December, 2008-February, 2009 period), as provided by the USDA (USDA, 2009).The USDA provides information on swine population in five different classes; breeding, under 60 lbs, 60-119 lbs, 120-179 lbs, and over 180 lbs. It was determined that the average weight of a breeding pig was 433 lbs (Williams, 2005). The under 60 lbs category was interpreted as representing feeder pigs, which is estimated to have an average weight of 30 lbs (Williams, 2005). For 60-119 lbs and 120-179 lbs the average of the weight range was used, i.e. 90 and 150 lbs. For the > 180 lbs category, 220 lbs was estimated to be the average pig weight. From this the total live animal weight for North Carolina was calculated, which is presented in Table 4.14. Using this and the overall average normalized emission (Table 4.9), the NMVOC barn emissions were estimated. The barn emissions, the lagoon emissions, and the total emissions (lagoon + barn) are presented in Table 4.15. Of the NMVOCs, ethanol has the largest North Carolina swine CAFO emissions with an emission of 206,367 kg yr^{-1}. The second highest was acetone with an emission of 134,765 kg yr^{-1}, which was closely followed by methanol with an emission of 134,732 kg yr^{-1}. The 4^{th} and 5^{th} highest are 2-3 butanedione and 4-methylphenol with emissions of 81,704 and 70,064 kg yr^{-1}, respectively. The next highest is acetaldehyde with an emission of 53,798 kg yr^{-1}. The other aldehyde compounds, MEK, hexane and 2-ethyl-1-hexanol had smaller emissions ranging from 5,867 to 16,519 kg yr^{-1}. With the exception of MEK, it can be observed that barns contribute 72.7% to ~100% of NMVOCs emissions in this study.

4.3.3.4. Ozone Potential

The potential for NMVOCs to form ozone was estimated by taking into account NMVOCs North Carolina emissions and their reaction rate with the hydroxyl radical (OH). Although this estimation technique does not give a complete representation of potential ozone production, it does provide an indicator of the VOCs that are most likely to contribute to the formation of ozone.

Reaction rates were normalized by propylene reaction rate as suggested by the National Research Council (NRC), (1991), therefore:

$$Ozone\,Potential = Emission(x)\left(\frac{k_{OH}(x)}{k_{OH}(p)}\right) \quad (3)$$

where x is the North Carolina emission of the NMVOC of interest in kg yr^{-1}, k_{OH} (x) is the reaction rate of the NMVOC of interest with OH , and k_{OH} (p) is the reaction rate of propylene with OH, which is 2.63 x 10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Atkinson and Arey, 2003). Table 4.16 presents the ozone potential of the significant NMVOCs measured in this study. For six of the NMVOCs (2-3 butanedione, 4-methylphenol, decanal, nonanal, octanal, and 2-ethyl-1-hexanol), the reaction rate with OH could not be found in literature.

Due to it's reaction rate with OH, acetaldehyde, which had the 6th largest emission, had the highest potential to form ozone, with a value of 32,320 kg yr^{-1}. Ethanol, which had the largest emissions, had the 2nd highest potential to form ozone with a value of 25,659 kg yr^{-1}. Hexanal and heptanal had the 3rd and 4th highest potential to form ozone, with values of 16,368 and 8,585 kg yr^{-1}, respectively. Hexanal and

heptanal had low emissions, but had the fastest reaction rates of the NMVOCs. As a result of their low reactivity, both methanol (4,836 kg yr^{-1}) and acetone (1,122 kg yr^{-1}), had low potentials to form ozone, despite their large emissions. Hexane also had a low potential for ozone formation (1,906 kg yr^{-1}), which was mostly due to low emissions. The lowest ozone potential was MEK (382 kg yr^{-1}), due to a combination of low emissions and low reactivity.

4.4. CONCLUSIONS

NMVOCs emissions were measured over four seasonal sampling periods from an anaerobic lagoon and barn at a swine CAFO in North Carolina. The NMVOC emissions were evaluated with respect to seasonal variations and the influence of the environmental parameters. The potential environmental impact of swine CAFO emissions was assessed in a number of ways. NMVOC barn exhaust concentrations were compared to their odor threshold. Also, hazardous air pollutants (HAPs) were identified in lagoon and barn samples. In addition, HAPs emissions were calculated. Average seasonal NMVOC emissions from the lagoon and barn were used to estimate total North Carolina swine CAFO emissions. The potential for NMVOCs to form ozone was also assessed.

12 significant compounds were identified in lagoon samples. Of the significant lagoon NMVOCs, three were alcohols (ethanol, 2-ethyl-1-hexanol, and methanol), six were aldehydes (acetaldehyde, decanal, heptanal, hexanal, nonanal and octanal), two were ketones (acetone and methyl ethyl ketone (MEK)), and one was a phenol (4-methylphenol). Overall average fluxes of these compounds ranged from 0.08 μg m^{-2} min^{-}

^{1} for 4-methylphenol to 2.11 μg m^{-2} min^{-1} for acetone. For seven of these 12 compounds (4-methylphenol, acetaldehyde, decanal, heptanal, hexanal, octanal and 2-ethyl-1-hexanol), pH was found to have the strongest relationship with flux. For all seven compounds, the relationship between pH and flux was negative. Three of the NMVOCs (methyl ethyl ketone, acetone and nonanal) were found to have their strongest relationship with lagoon temperature, with fluxes increasing as lagoon temperature increased. One NMVOC (methanol) was found to have it's strongest relationship with air temperature. Similarly to lagoon temperature, the relationship was positive. Ethanol was the only compound not to have any significant relationships with environmental parameters.

In barn samples, six significant compounds were identified, two alcohols (methanol and ethanol), two ketones (acetone and 2-3 butanedione), an aldehyde (acetaldehyde) and a phenol (4-methylphenol). Overall average concentrations for these six compounds ranged from 2.87 ppb for 4-methylphenol to 16.12 ppb for ethanol. Ethanol also had the highest normalized overall average emission rate, with an emission of 0.45 g day^{-1} AU^{-1}. The lowest normalized overall average emission rate was acetaldehyde with an emission of 0.16 g day^{-1} AU^{-1}. As a result of the nature of the barn environment, it is hard to determine the effect of environmental parameters on NMVOC emissions, however, one NMVOC, ethanol had a weak significant relationship with barn temperature.

Eight odorous compounds were identified in barn samples. Of these eight, four had concentrations that exceeded an odor threshold. 4-methylphenol was the compound

that exceeded it's odor thresholds the most frequently and by the largest magnitude. Four of the significant NMVOCs emitted from lagoons and barns were also hazardous air pollutants (HAPs). These were acetaldehyde, methanol, 4-methylphenol and methyl ethyl ketone. Additionally, there were a further eight HAPs identified in lagoon and barn samples (benzene, ethyl benzene, hexane, methyl chloride, styrene, xylene, toluene and 2,2,4 trimethylpentane).

Using overall average lagoon flux and overall average barn emissions, the NMVOC swine CAFO emissions for North Carolina were calculated. The NMVOC with the largest North Carolina swine CAFO emissions was ethanol with an emission of 206,367 kg yr^{-1}. For all but one NMVOC, the barns composed the majority of North Carolina swine CAFO emissions in this study, with contributions ranging from 72.7% to ~100%. NMVOCs were evaluated for their potential to form ozone by taking into account their emissions and their reaction rate with the hydroxyl radical (OH). From this, acetaldehyde was identified as the NMVOC with the highest potential to form ozone.

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Table 4.1. Time (EST) and frequency of canister sampling.

		Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Total number of samples
Lagoon	Summer	17:40	15:23	15:20	10:51	15:07	13:41	10:58	10
							13:52	11:07	
								11:16	
	Fall	16:30	14:01	16:25	15:33	15:24			10
				16:42	16:01	15:34			
						15:43			
						16:00			
	Winter	16:28	14:25	15:45	10:31				11
		16:41	14:36	16:01	10:42				
		16:50		16:32	10:52				
	Spring	12:36	11:50	15:08	12:37				10
		12:45	11:59	15:17	12:48				
		12:57	12:08						
Barn	Summer	12:24	14:40	14:12	8:36				10
			14:49	14:21	8:50				
			14:59		8:59				
			15:08						
	Fall	15:35	14:02	15:30	15:23				10
			14:19	16:01	15:34				
				16:15	15:44				
				16:25					
	Winter	14:32	12:56	13:43	12:58				9
		14:43	13:09	14:03	13:07				
				14:30					
	Spring	14:33	12:09	13:16	15:10	11:53			9
		14:45		13:25	15:21	12:01			

Table 4.2. Seasonal NMVOC fluxes and their overall seasonal fluxes.

	Flux ($\mu g\ m^{-2}\ min^{-1}$)				
	Summer	Fall	Winter	Spring	Overall Average
Acetaldehyde	1.67[a] (1.20)[b] n = 10[c]	0.40 (0.14) n = 10	0.34 (0.19) n = 11	0.24 (0.10) n = 10	0.66
Acetone	4.41 (1.26) n = 10	1.00 (0.31) n = 10	1.19 (0.20) n = 11	1.82 (0.84) n = 10	2.11
Decanal	0.21 (0.10) n = 10	0.07 (0.03) n = 10	0.09 (0.07) n = 11	0.06 (0.03) n = 10	0.11
Ethanol	0.55 (0.37) n = 10	0.26 (0.16) n = 10	1.54 (3.78) n = 11	0.02 (0.01) n = 10	0.59
2-ethyl-1-hexanol	0.54 (0.66) n = 10	0.06 (0.02) n = 10	0.06 (0.07) n = 11	0.06 (0.02) n = 10	0.18
Heptanal	0.27 (0.31) n = 10	0.06 (0.04) n = 10	0.06 (0.03) n = 10	0.05 (0.02) n = 10	0.11
Hexanal	0.31 (0.15) n = 7	0.11 (0.04) n = 6	0.08 (0.05) n = 9	0.07 (0.02) n = 9	0.14
Methanol	1.39 (1.15) n =10	1.53 (0.41) n = 6	0.67 (0.23) n = 11	1.16 (0.84) n = 10	1.19
MEK	0.97 (0.22) n = 10	0.42 (0.14) n = 10	0.41 (0.16) n = 11	0.42 (0.06) n = 10	0.56
4-methylphenol	0.17 (0.08) n = 10	0.03 (0.02) n = 10	0.06 (0.04) n =11	0.04 (0.03) n = 10	0.07
Nonanal	0.29 (0.29) n = 10	0.06 (0.04) n = 10	0.09 (0.09) n = 11	0.06 (0.02) n = 10	0.13
Octanal	0.30 (0.34) n = 10	0.06 (0.04) n = 10	0.07 (0.05) n = 11	0.05 (0.02) n = 10	0.12

[a] Mean value
[b] ±1 standard deviation
[c] Number of samples

Table 4.3. Seasonal environmental parameters for canister samples.

Season	Lagoon Temperature (^{o}C)	Lagoon pH	Air Temperature (^{o}C)	Wind Speed (m/s)
Summer	27.00[a] (3.34)[b]	7.33 (0.16)	26.74 (3.32)	2.23 (0.87)
	n = 10[c]	n = 5	n = 10	n = 10
Fall	23.27 (1.67)	7.63 (0.16)	25.49 (3.01)	3.07 (2.03)
	n = 10	n = 10	n= 10	n = 10
Winter	12.34 (2.50)	8.08 (0.11)	8.59 (1.23)	2.38 (0.77)
	n = 11	n= 11	n=11	n= 11
Spring	19.59 (1.77)	8.03 (0.07)	18.30 (6.24)	4.37 (1.80)
	n = 10	n = 10	n = 10	n = 10

[a] Mean value

[b] ±1 standard deviation

[c] n is the number of observations

Table 4.4. r^2 and p-values for the relationship between NMVOC lagoon fluxes and environmental parameters.

	Lagoon Temperature		Lagoon pH		Air Temperature	
	r^2	p-value	r^2	p-value	r^2	p-value
Acetaldehyde	0.16	0.01	0.32	<0.01	0.15	0.10
Acetone	0.32	<0.01	0.20	<0.01	0.16	0.01
Decanal	0.13	0.02	0.19	0.01	0.07	0.10
Ethanol	0.04	0.21	0.01	0.64	0.04	0.22
2-ethyl-1-hexanol	0.14	0.02	0.26	< 0.01	0.08	0.07
Heptanal	0.10	0.05	0.23	< 0.01	0.07	0.09
Hexanal	0.26	< 0.01	0.42	< 0.01	0.25	< 0.01
Methanol	0.15	0.02	< 0.01	0.85	0.29	< 0.01
MEK	0.33	<0.01	0.32	< 0.01	0.23	< 0.01
Nonanal	0.10	0.04	0.09	0.08	0.07	0.10
Octanal	0.10	0.04	0.19	< 0.01	0.08	0.08

Table 4.5. NMVOC concentrations from swine CAFO barns.

	Concentration (ppb)					
	Acetaldehyde	Acetone	2-3 butanedione	Ethanol	Methanol	4-methylphenol
Summer	1.44[a]	2.03	2.33	12.85	6.84	0.95
	(2.21)[b]	(2.72)	(3.04)	(15.28)	(6.29)	(1.11)
	n = 10[c]	n = 10	n = 10	n = 10	n = 10	n =10
Fall	7.20	10.29	6.23	14.15	20.33	2.37
	(6.59)	(4.30)	(6.22)	(7.81)	(11.35)	(2.50)
	n = 10	n = 10	n = 10	n = 10	n = 9	n = 10
Winter	2.39	7.31	1.36	8.67	14.17	2.91
	(4.86)	(4.49)	(2.08)	(15.89)	(12.32)	(4.31)
	n = 9	n = 9	n = 9	n = 9	n = 9	n = 9
Spring	6.54	12.85	4.33	28.80	19.18	5.25
	(2.32)	(4.89)	(2.30)	(7.33)	(5.89)	(1.73)
	n = 9	n = 9	n = 9	n = 9	n = 9	n = 9
Overall average concentration	4.17	8.12	3.56	16.12	15.13	2.87

[a] Mean value
[b] ±1 standard deviation
[c] Number of samples

Table 4.6. NMVOCs concentrations from previous swine CAFO barn studies (ACE =Acetaldehyde, ACT = Acetone, 2-3 B = 2-3 butanedione , ETH = Ethanol, MET = Methanol, 4-MP = 4-methylphenol).

Reference	Location	Vent System	Manure collection system/description of sample location	Production type	Month	Concentration (ppb)					
						ACE	ACT	2-3 B	ETH	MET	4-MP
Schiffman et al. (2001)	NC	NS	NS/ inside barn	NS	NS	4.0	1	-[a]	-[a]	-[a]	9
Blunden et al. (2005)	NC	N	Shallow pit/ outside of barn near fan	Finish	Sep	2.1	13.7	-	45.1	21.6	5.0
Blunden et al. (2005)	NC	N	Shallow pit/ outside of barn near fan	Finish	Jan	1.2	0.1	-	0.5	1.2	0
Blunden et al. (2005)	NC	M	Shallow pit/ outside of barn near fan	Finish	Oct	3.6	1.5	-	1.0	3.0	0
Blunden et al. (2005)	NC	M	Shallow pit/ outside of barn near fan	Finish	Feb	1.8	1.7	-	12.5	9.0	1.6
Trabue et al. (2008)	IA	M	Shallow pit/inside barn	Finish	NS[b]	-	-	-	-	-	2.4
This study	NC	M	Shallow pit/barn fan	Finish	June	1.4	2.0	2.3	12.8	6.8	1.0
This study	NC	M	Shallow pit/barn fan	Finish	Oct-Nov	7.2	10.3	6.2	14.1	20.3	2.4
This study	NC	M	Shallow pit/barn fan	Finish	Feb	2.4	7.3	1.4	8.7	14.2	2.9
This study	NC	M	Shallow pit/barn fan	Finish	Apr	6.5	12.9	4.3	28.8	19.2	5.2

NS = not specified, N = naturally ventilated, M= mechanically ventilated

[a] Compound identified, but concentration not reported.

[b] Barn temperature was reported as 15^{o}C.

Table 4.7. Ventilation rate and corresponding environmental parameters during canister sampling.

Season	Ventilation rate (m^3 min^{-1})	Barn Temperature (^oC)	Ambient Temperature (^oC)
Summer	2040	30.27	31.15
	(589)	(3.18)	(2.48)
	n =10	n = 10	n = 10
Fall	725	16.42	23.70
	(289)	(3.67)	(1.81)
	n = 10	n = 10	n = 10
Winter	435	14.05	19.78
	(296)	(4.15)	(2.78)
	n = 9	n = 9	n = 9
Spring	850	22.42	27.61
	(366)	(3.47)	(1.62)
	n = 9	n = 9	n = 9

Table 4.8. Seasonal emissions of NMVOCs.

	Emission (g day^{-1})					
	Acetaldehyde	Acetone	2-3 butanedione	Ethanol	Methanol	4-methylphenol
Summer	5.07[a]	9.58	16.60	55.33	22.25	9.05
	(6.79)[b]	(11.12)	(17.62)	(44.98)	(16.36)	(8.25)
Fall	13.92	24.96	22.93	28.40	26.92	10.90
	(11.91)	(11.92)	(21.57)	(19.73)	(21.62)	(14.77)
Winter	1.78	9.10	2.04	6.71	11.32	5.43
	(3.62)	(7.41)	(2.99)	(12.25)	(14.87)	(7.75)
Spring	11.12	34.85	18.00	61.34	28.46	28.22
	(4.08)	(12.63)	(13.17)	(17.98)	(9.23)	(14.67)
Overall average emissions	7.97	19.62	14.89	37.95	22.24	13.40

[a] Mean value

[b] ±1 standard deviation

Table 4.9. Seasonal pig production information and the calculated normalized NMVOCs emission rates (ACE =Acetaldehyde, ACT = Acetone, 2-3 B = 2-3 butanedione , ETH = Ethanol, MET = Methanol, 4-MP = 4-methylphenol).

Sampling Season	Number of Pigs	Number of weeks in rotation	Average Weight (kg)	Total Live Animal Weight (kg)	Normalized Emissions (g day^{-1} AU^{-1})					
					ACE	**ACT**	**2-3 B**	**ETH**	**MET**	**4-MP**
Summer	884.5	7-8	48.7	43,049	0.06[a]	0.11	0.19	0.64	0.26	0.11
					(0.08)[b]	(0.13)	(0.20)	(0.52)	(0.19)	(0.10)
Fall	994.5	4-5	34.6	34,428	0.20	0.36	0.33	0.41	0.39	0.16
					(0.17)	(0.17)	(0.31)	(0.29)	(0.31)	(0.21)
Winter	476	20-21	116.6	55,513	0.02	0.08	0.02	0.06	0.10	0.05
					(0.03)	(0.07)	(0.03)	(0.11)	(0.13)	(0.07)
Spring	874.5	8-9	50.6	44,262	0.13	0.39	0.20	0.69	0.32	0.32
					(0.05)	(0.14)	(0.15)	(0.20)	(0.10)	(0.17)
Overall average emissions					0.10	0.24	0.19	0.45	0.27	0.16

[a] Mean value

[b] ±1 standard deviation

Table 4.10. NMVOCs seasonal and average seasonal concentration, emissions and normalized emissions.

		Decanal	2-ethyl-1-hexanol	Heptanal	Hexanal	Nonanal	Octanal
Summer	Concentration (ppb)	0.03[a] (0.06)[b]	0.24 (0.28)	0.09 (0.07)	0.26(0.15)	0.19 (0.12)	0.10 (0.11)
	Emission (g day^{-1})	0.57 (1.26)	4.23 (5.25)	1.28 (1.00)	3.36 (2.42)	2.92 (1.64)	1.55 (1.39)
	Emission (g day^{-1} AU^{-1})	0.007 (0.015)	0.049 (0.061)	0.015 (0.012)	0.039 (0.028)	0.034(0.019)	0.018 (0.016)
	Number of samples	n = 10	n = 10	n = 9	n = 9	n = 10	n = 9
Fall	Concentration (ppb)	0.28 (0.48)	0.27 (0.24)	0.23 (0.19)	0.49 (0.33)	0.48 (0.45)	0.17 (0.09)
	Emission (g day^{-1})	1.53(1.91)	1.56 (1.30)	1.18 (1.20)	2.08 (1.55)	2.75 (2.68)	0.93 (0.66)
	Emission (g day^{-1} AU^{-1})	0.022 (0.028)	0.023 (0.019)	0.017 (0.017)	0.030 (0.022)	0.040 (0.039)	0.013 (0.010)
	Number of samples	n = 10	n = 10	n = 9	n = 10	n = 10	n = 10
Winter	Concentration (ppb)	0.10 (0.06)	0.09 (0.12)	0.11 (0.14)	0.37 (0.51)	0.29 (0.30)	0.07 (0.07)
	Emission (g day^{-1})	0.51(0.63)	0.21 (0.27)	0.22 (0.26)	0.62 (0.86)	1.15 (1.67)	0.19 (0.15)
	Emission (g day^{-1} AU^{-1})	0.005 (0.006)	0.002 (0.002)	0.002 (0.002)	0.006 (0.008)	0.010 (0.015)	0.002 (0.001)
	Number of samples	n = 9	n = 9	n = 9	n = 9	n = 9	n = 9
Spring	Concentration (ppb)	0.08 (0.11)	0.33 (0.24)	0.34 (0.18)	0.78 (0.36)	0.64 (0.50)	0.17(0.17)
	Emission (g day^{-1})	0.54 (0.65)	2.58 (2.55)	1.77 (0.64)	3.30 (1.36)	4.42 (3.48)	0.92 (0.73)
	Emission (g day^{-1} AU^{-1})	0.006 (0.007)	0.029 (0.029)	0.020 (0.007)	0.037 (0.015)	0.050 (0.039)	0.010 (0.008)
	Number of samples	n = 9	n = 9	n = 8	n =8	n = 9	n = 9
Overall average concentration (ppb)		0.12	0.23	0.19	0.48	0.40	0.13
Overall average emission (g day^{-1})		0.79	2.14	1.11	2.34	2.81	0.90
Overall average emission (g day^{-1} AU^{-1})		0.010	0.026	0.013	0.028	0.034	0.011

[a] Mean value

[b] ±1 standard deviation

Table 4.11. Odor threshold and characteristic of odorous NMVOCs.

Compound	**Odor Threshold (ppb)**	**Odor Characteristic**
Heptanal	4.79[1], 53.5[2]	Fruit, heavy[4], sweet, estery[5]
Octanal	1.35[1], 1.11-2.59[2]	Aldehydic[5]
Nonanal	2.24[1], 0.77-2.08[2]	Earthy, aldehydic[5]
Decanal	0.89[1]	ND
Ethylbenzene	2.88[1]	ND
2-3-Butanedione	4.37[1], 1.42-7.39[2]	Chlorine like, butter like[4]
4-methylphenol	1.86[1], 0.06793-0.264[2]	Medicinal, phenolic, barnyard
Hexanal	13.8[1], 7.0 -12.9[2]	Grassy[5]

ND = No Description of odor characteristic

[1] Devos et al. (1990)

[2] Rychlik et al. (1998)

[3] Haz -Map (2009)

[4] Schiffman et al., (2001)

[5] Cai et al., (2006)

Table 4.12. A comparison of NMVOC barns concentrations to their odor thresholds

Compound	**Odor threshold (ppb)**	Number of samples exceeding odor threshold			
		Summer	Fall	Winter	Spring
2-3 butanedione	**1.42**	4[a] Y	8 Y	3 N	8 Y
		8.57[b]	22.28	6.58	7.92
	4.37	2 N	6 Y	1 N	5 N
	7.39	1 N	2 N	0	1 N
Decanal	**0.89**	0	1 N	0	0
		0.18	1.63	0.21	0.34
Heptanal	**4.79**	0	0	0	0
		0.20	0.53	0.35	0.74
Hexanal	**7.0**	0	0	0	0
		0.55	1.07	1.50	1.49
4-methylphenol	**0.06793**	9 Y	10 Y	6 Y	9 Y
		3.12	7.67	11.67	8.06
	0.264	5 Y	7 Y	5 Y	9 Y
	1.86	2 N	5 Y	3 Y	9 Y
Octanal	**1.11**	0	0	0	0
		0.31	0.34	0.18	0.53
Nonanal	**0.77**	0	3 N	0	3 N
		0.35	1.26	0.73	1.70

[a] If there are individual samples exceeding the odor threshold, the letter indicates if the seasonal average exceeds the odor threshold, Y = Yes, N = No

[b] Highest individual sample concentration observed in each season

Table 4.13. Hexane seasonal and overall average concentrations, emissions and normalized emissions.

	Concentration (ppb)	Emissions ($g\ day^{-1}$)	Emissions ($g\ day^{-1}\ AU^{-1}$)
Summer	0.08	0.74	0.009
	(0.05), n = 10	(0.42)	(0.005)
Fall	0.29	1.19	0.017
	(0.20), n = 10	(1.07)	(0.016)
Winter	1.20	2.29	0.021
	(0.86), n = 9	(1.42)	(0.013)
Spring	0.96	3.69	0.042
	(0.37), n = 9	(1.33)	(0.015)
Overall	0.63	1.98	0.022

Table 4.14. Live animal weight calculations for the state of North Carolina for the December, 2008 – February, 2009 period.

	Average Weight (lb)	Number	Total Weight (lb)
Breeding	433	980,000	$4.24 * 10^8$
< 60 lbs	30	3,300,000	$9.90 * 10^7$
60-119 lbs	90	1,930,000	$1.74 * 10^8$
120-179 lbs	150	1,750,000	$2.63 * 10^8$
>180 lbs	220	1,640,000	$3.61 * 10^8$
Total live animal weight (lbs)			$1.32* 10^9$
Total live animal weight (kg)			$5.99* 10^8$

Table 4.15. Lagoon, barn and total NC NMVOC swine CAFO emissions

Compound	NC lagoon emissions (kg yr^{-1})	% lagoon contribution to total emissions	NC barn emissions (kg yr^{-1})	% barn contribution to total emissions	Total NC swine CAFO emissions (kg yr^{-1})
Methanol	17,464	13.0	117,268	87.0	134,732
MEK	8,208	~ 100	NQ	-	8,208
Ethanol	8,701	4.2	197,666	95.8	206,367
4-methylphenol	1,097	1.6	68,967	98.4	70,064
Acetaldehyde	9,782	18.2	44,016	81.8	53,798
Acetone	30,983	23.0	103,781	77.0	134,765
Decanal	1,548	26.4	4,319	73.6	5,867
Heptanal	1,632	21.7	5,894	78.3	7,526
Hexanal	2,089	14.6	12,260	85.4	14,349
Nonanal	1,861	11.3	14,658	88.7	16,519
2-3 butanedione	NQ	-	81,704	~ 100	81,704
Hexane	NQ	-	8,744	~ 100	8,744
Octanal	1,795	27.3	4,771	72.7	6,567
2-Ethyl-1-hexanol	2,616	18.9	11,232	81.1	13,848

NQ = Not quantified.

Table 4.16. NMVOCs ozone potential.

	Emission ($kg\ yr^{-1}$)	Reaction rate ($cm^3\ molecule^{-1}\ s^{-1}$)	Propylene normalized reaction rate	Ozone potential ($kg\ yr^{-1}$)
Methanol	134,732	$9.44 * 10^{-13}$ [a]	0.036	4,836
Ethanol	206,367	$3.27 * 10^{-12}$ [a]	0.124	25,659
Acetaldehyde	53,798	$1.58 * 10^{-11}$ [a]	0.600	32,320
Acetone	134,765	$2.19 * 10^{-13}$ [a]	0.008	1,122
Heptanal	7,526	$3.00 * 10^{-11}$ [b]	1.141	8,585
Hexanal	14,349	$3.00 * 10^{-11}$ [b]	1.141	16,368
Hexane	9,642	$5.20 * 10^{-12}$ [b]	0.198	1,906
MEK	8,241	$1.22 * 10^{-12}$ [b]	0.046	382

[a] reaction rate from Atkinson, (1994)

[b] reaction rate from Atkinson and Arey, (2003)

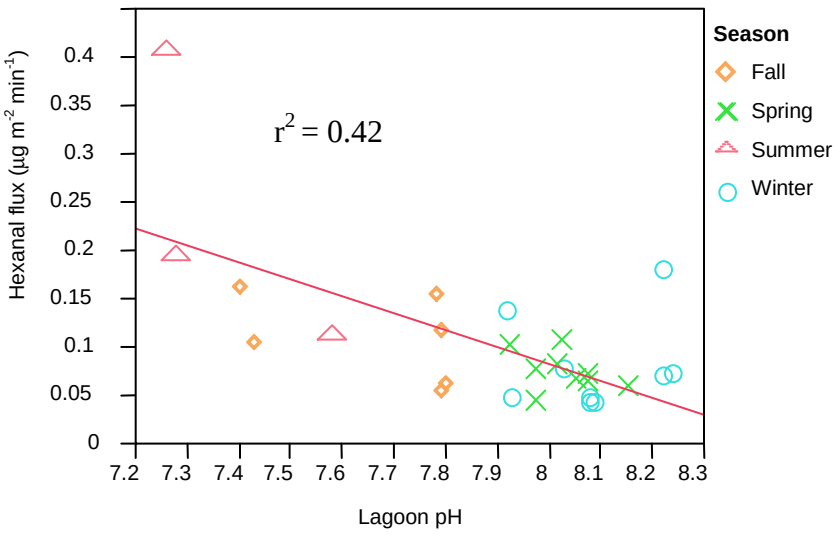

Figure 4.1. The relationship between hexanal flux (µg m^{-2} min^{-1}) and lagoon pH.

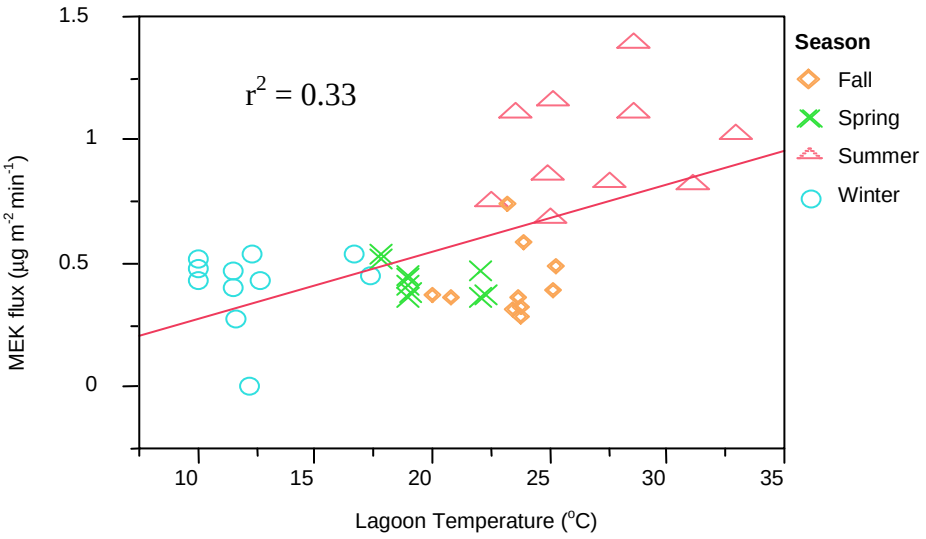

Figure 4.2. The relationship between MEK flux (µg m^{-2} min^{-1}) and lagoon temperature (^{o}C).

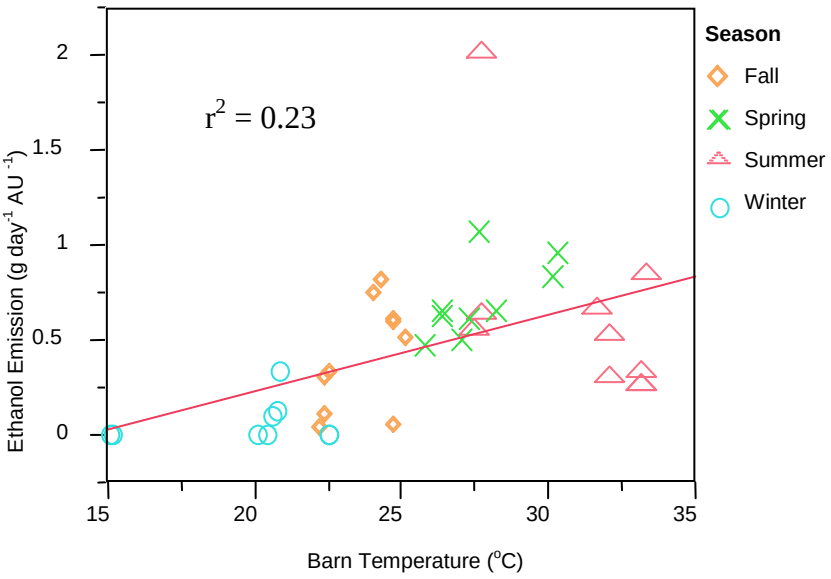

Figure 4.3. The relationship between ethanol emissions and barn temperature (^{o}C).

CHAPTER V. SUMMARY AND CONCLUSIONS

Measurements of reduced sulfur compounds (RSCs) and non-methane volatile organic compounds (NMVOCs) were made from an anaerobic lagoon and barn at a swine concentrated animal feeding operation (CAFO) in North Carolina.

H_2S emissions were measured continuously and were evaluated with respect to diurnal and seasonal variations, as well as the influence of environmental parameters. The overall average H_2S lagoon flux was 1.33 $\mu g\ m^{-2}\ min^{-1}$. Lagoon pH was found to have the largest influence on H_2S flux, followed by lagoon temperature and wind speed. The seasonal H_2S barn concentrations were found to range from 72 ± 43 ppb in the summer to 631 ± 240 ppb in the spring. Overall average seasonal normalized barn emissions were 3.3 $g\ day^{-1}\ AU^{-1}$ for H_2S. Barn temperature was found to have a weak correlation with H_2S emissions.

In addition, a process based air-manure interface mass transfer model was developed to predict H_2S manure emissions. Different approaches based on thermodynamic principles and related published information were used to determine the three main components of the model: the overall mass transport coefficient, the dissociation constant, and the Henry's law constant. The accuracy of this model was evaluated by comparing predicted H_2S fluxes to measured H_2S lagoon fluxes.

The process based air-manure interface mass transfer model did well in predicting H_2S fluxes, when compared with 15 minute average lagoon fluxes ($r^2 = 0.57$, $p<0.0001$). The model also performed well in predicting seasonal lagoon fluxes. It is hypothesized

that with good estimations of the overall mass transport coefficient, that this model could be applied to predict trace gas CAFO emissions from a variety of manure surfaces, thus providing a method for quantifying emissions in different production, management and environmental conditions.

RSCs (excluding H_2S) and NMVOC emissions were measured using passivated canisters. Nine to eleven canister samples were taken each from both the anaerobic lagoon and barn in each sampling period. These emissions were evaluated with respect to seasonal and environmental factors. The two main RSCs identified in lagoon and barn samples were dimethyl sulfide (DMS) and dimethyl disulfide (DMDS). Overall average seasonal DMS and DMDS lagoon fluxes were over an order of magnitude lower than the H_2S flux, 0.12 and 0.09 $\mu g\ m^{-2}\ min^{-1}$, respectively. DMS and DMDS fluxes were found to be influenced by different environmental parameters. DMS flux was significantly influenced by pH, whereas DMDS was significantly influenced by lagoon temperature. For DMS and DMDS, the seasonal barn concentrations ranged from 0.17-0.89 and 0.46-0.96 ppb, respectively. The overall average barn emissions for DMS and DMDS were 0.018 g day^{-1} AU^{-1} and 0.037 g day^{-1} AU^{-1}, respectively. These were approximately two orders of magnitude less than the corresponding H_2S emissions. DMS and DMDS emissions had little or no correlation with barn temperature.

12 significant NMVOCs were identified in lagoon samples. Of the significant lagoon NMVOCs, three were alcohols (ethanol, 2-ethyl-1-hexanol, and methanol), six were aldehydes (acetaldehyde, decanal, heptanal, hexanal, nonanal and octanal), two were ketones (acetone and methyl ethyl ketone (MEK)), and one was a phenol (4-

methylphenol). Overall average fluxes of these compounds ranged from 0.08 μg m^{-2} min^{-1} for 4-methylphenol to 2.11 μg m^{-2} min^{-1} for acetone. For seven of these 12 compounds (4-methylphenol, acetaldehyde, decanal, heptanal, hexanal, octanal and 2-ethyl-1-hexanol), pH was found to have the strongest relationship with flux. For all seven compounds, the relationship between pH and flux was negative. Three of the NMVOCs (methyl ethyl ketone, acetone and nonanal) were found to have their strongest relationship with lagoon temperature, with fluxes increasing as lagoon temperature increased. One NMVOC (methanol) was found to have it's strongest relationship with air temperature. Similarly to lagoon temperature, the relationship was positive. Ethanol was the only compound not to have any significant relationships with environmental parameters.

In barn samples, six significant compounds were identified, two alcohols (methanol and ethanol), two ketones (acetone and 2-3 butanedione), an aldehyde (acetaldehyde) and a phenol (4-methylphenol). Overall average seasonal concentrations for these six compounds ranged from 2.87 ppb for 4-methylphenol to 16.12 ppb for ethanol. Ethanol also had the highest overall average normalized emission rate, with an emission rate of 0.45 g day^{-1} AU^{-1}. The lowest normalized overall average emission rate was acetaldehyde with an emission of 0.16 g day^{-1} AU^{-1}. None of the NMVOCs, except for ethanol had a significant relationship with barn temperature.

The potential environmental impacts of RSC and NMVOC emissions were assessed by comparing barn exhaust concentrations to their odor threshold, identifying

the number of hazardous air pollutants (HAPs), estimating total North Carolina swine CAFO emissions, and for NMVOCs, assessing their potential to form ozone.

H_2S barn concentrations were found to exceed four different published odor thresholds by one to two orders of magnitude. No DMS concentrations exceeded their odor threshold. DMDS concentrations were found to regularly exceed an odor threshold.

Eight odorous NMVOCs were identified in barn samples. Of these eight, four had concentrations that exceeded an odor threshold. 4-methylphenol was the compound that exceeded it's odor thresholds the most frequently and by the largest magnitude.

The identification of compounds at concentrations above their odor threshold at the barn fans indicates that there may be potential health effects for swine CAFO workers. However, to assess the potential health effects for people who live in the surrounding area, the dispersion of the odorous pollutants needs to be modeled. This would allow an estimation of the distance from the swine CAFO that compounds remain odorous. From this, the extent to which odorous compounds cross over the swine CAFO property boundary into the surrounding environment could be evaluated.

There were 12 HAPs identified in lagoon and barn samples. Four were significant NMVOCs (acetaldehyde, methanol, 4-methylphenol and MEK); the other eight were benzene, ethyl benzene, hexane, methyl chloride, styrene, xylene, toluene and 2,2,4 trimethylpentane. However, further evaluation is needed to assess potential health problems associated with the emission of HAPs from swine CAFOs.

Using overall average lagoon and barn emissions, the emissions from swine CAFOs in North Carolina were estimated. RSC emissions from swine CAFOs in North

Carolina were estimated to be 1.46 million kg yr^{-1} for H_2S, 9,509 kg yr^{-1} for DMS, and 17,406 kg yr^{-1} for DMDS. H_2S swine CAFO emissions were estimated to contribute ~21% of total North Carolina H_2S emissions. To assess the potential regional effect of these RSC emissions, the formation of fine particulate matter (PM_{fine}) from RSCs and in particular H_2S needs to be modeled.

The NMVOC with the largest North Carolina swine CAFO emissions was ethanol with an emission of 206,367 kg yr^{-1}. The second highest was acetone with an emission of 134,765 kg yr^{-1}, which was closely followed by methanol with an emission of 134,732 kg yr^{-1} NMVOCs were evaluated for their potential to form ozone by taking into account their emissions and their reaction rate with the hydroxyl radical (OH). From this, acetaldehyde was identified as the NMVOC with the highest potential to form ozone.