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Characterizing ammonia and hydrogen sulfide emissions from a swine waste treatment lagoon in North Carolina

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Abstract

Emissions of atmospheric ammonia–nitrogen (NH_3-N, where $NH_3\text{-N} = (14/17)NH_3$) and hydrogen sulfide ($H_2S$) from a commercial anaerobic swine waste treatment lagoon (17,150 m^2 at normal liquid level) were measured over a 1-year period. Continuous simultaneous measurements were made at the lagoon using a dynamic flow-through chamber system for ~1 week during four seasons, October–November 2004 (fall), February 2005 (winter), April 2005 (spring), and June 2005 (summer) in an effort to examine diurnal and seasonal variability, and the respective relationships of NH_3-N and H_2S emissions to lagoon physicochemical properties. Continuously measured lagoon physicochemical parameters include lagoon surface temperature and lagoon pH. Aqueous lagoon samples were collected daily and analyzed for total Kjeldahl nitrogen (TKN), total ammoniacal nitrogen (TAN), and total sulfide concentration. TKN, TAN, and sulfide concentrations ranged from 400–650, 360–590, and 0.1–13.0 $mg\,L^{-1}$, respectively. For NH_3-N, the largest fluxes were observed during the summer ($>4200\,\mu g\,N\,m^{-2}\,min^{-1}$). During the fall and spring, average NH_3-N fluxes were 1634 ± 505 and $>2495\,\mu g\,N\,m^{-2}\,min^{-1}$, respectively. The lowest fluxes were observed during the winter where average flux values were $1290 \pm 246\,\mu g\,N\,m^{-2}\,min^{-1}$. Fluxes for H_2S were negligible during the winter season. Average fluxes increased during the fall ($0.3 \pm 0.1\,\mu g\,m^{-2}\,min^{-1}$) and spring ($0.5 \pm 1.0\,\mu g\,m^{-2}\,min^{-1}$), and highest flux values were observed during the summer ($5.3 \pm 3.2\,\mu g\,m^{-2}\,min^{-1}$). The seasonal NH_3-N and H_2S emission factors ranged from ~10 to ~40 $kg\,N\,AU^{-1}\,yr^{-1}$ (1 AU = 500 kg live animal weight) and ~0 to ~0.05 $kg\,H_2S\,AU^{-1}\,yr^{-1}$, respectively. Generally, the lagoon emissions for H_2S were ~3–4 orders of magnitude less than NH_3-N. The gas fluxes were related to various physicochemical parameters including the pH and near-surface temperature of the lagoon, and the aqueous concentration of the respective gas.

Keywords: Ammonia; Hydrogen sulfide; Emissions; Dynamic chamber; Pig manure; Lagoon

1. Introduction

Emissions of potentially harmful gases, such as ammonia (NH_3) and hydrogen sulfide (H_2S), from confined animal feeding operations (CAFOs) have become a major problem in recent years in North Carolina as changes in crop and livestock production methods are in turn changing emissions of trace gases (e.g., sulfur and nitrogen species) into the atmosphere (Aneja et al., 2006a). Notably, the swine industry has grown significantly since the early 1990s, with an increase in inventory from 2.5 million

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to ~10 million animals, and is now a major animal agricultural industry in the state. Public concerns about potential environmental and health effects of air emissions from CAFOs have increased in parallel with the growth and consolidation of this industry (Aneja et al., 2006a).

Ammonia is a by-product of microbial decomposition of the organic nitrogen compounds in manure. It also occurs as absorbed nitrogen in the form of organically bound nitrogen, and as urea in urine (US EPA, 2001). Ammonia released from near-surface sources (i.e., waste treatment lagoons) into the atmosphere generally has a relatively short lifetime of ~1–5 days (Warneck, 2000) and may deposit near the source through dry or wet deposition. However, ammonia can also participate in atmospheric reactions (e.g., gas-to-particle conversion) once airborne, forming ammonium aerosols such as ammonium sulfate, -nitrate, -chloride, which tend to have longer atmospheric residence lifetimes (~1–15 days) owing to a decrease in dry deposition velocity (Aneja et al., 1998) and therefore, may be transported and deposited further downwind from the source. An environmental concern in eastern North Carolina that has been associated with ammonium aerosols is the deposition into sensitive coastal river and coastal ecosystems where nitrogen loading may lead to soil acidification, enhanced eutrophication, and the growth in both frequency and magnitude of harmful algal blooms, which may in turn upset ecosystem nutrient balances (Paerl, 1997).

Hydrogen sulfide, another major compound of concern, is a colorless, potentially lethal gas released from swine manure (US EPA, 2003). It is produced as manure decomposes anaerobically, resulting from the mineralization of organic sulfur compounds as well as the reduction of oxidized inorganic sulfur compounds such as sulfate by sulfur-reducing bacteria (US EPA, 2001). The US Center for Disease Control (CDC) warns that brief exposures to high concentrations (>500 ppm, parts per million) can cause unconsciousness or death (ATSDR, 2004). Campagna et al. (2004) have reported a correlation between elevated ambient H_2S concentrations and hospital visits for respiratory diseases. Donham et al. (1982) reported that hydrogen sulfide appeared to be the main toxic substance in liquid manure associated with death and illness for people with acute exposure to gases emanating from liquid manure. With a low odor threshold ranging from 0.0005 to 0.3 ppm (ATSDR, 2004), it is also one of the primary gases released from swine facilities that is associated with odor complaints due to its characteristic "rotten egg" smell.

Significant efforts have been devoted to understanding emissions of ammonia from manure storage facilities (Aneja et al., 2000, 2001a, b; Harper et al., 2000; Zahn et al., 2001, Lim et al., 2003). Arogo et al. (2003) have reviewed measurement techniques and studies undertaken to estimate NH_3 emissions from both swine lagoons and animal confinement houses. Emissions of hydrogen sulfide from animal confinement houses have been estimated (Zhu et al., 2000; Ni et al., 2002) and a few studies have reported emissions from waste storage treatment lagoons (Zahn et al., 2001; Lim et al., 2003; Byler et al., 2004). However, none of the H_2S lagoon emissions were estimated from farms in the southeastern US. Various factors, such as differing animal and crop production, farming activities, and regional climates, may affect the emissions of gases into the atmosphere. Emissions estimates generated for one set of manure storage facilities may not translate readily to others. It is therefore important for comprehensive emissions measurements to be made from different types and locations of manure storage facilities in order to develop accurate emission factors.

The primary objective of this research initiative was to investigate and evaluate the variability of ammonia and hydrogen sulfide emissions with respect to diurnal and seasonal variations as well as the influence of meteorological and physicochemical factors. Data presented here was collected continuously using in situ measurement techniques for a 1-week period during each season (i.e., fall, winter, spring, summer) for one year from an anaerobic swine lagoon at a finishing hog farm in eastern North Carolina. The approach in the analysis of the data (i.e., the relationship of the NH_3-N and H_2S emissions with physicochemical properties of the system) may offer an opportunity to translate the results to other systems.

2. Methods and materials

2.1. Physiographic location and farm description

The experimental site is an approximately 7000 head operational commercial swine finishing farm, located in Jones County, North Carolina in the southeastern coastal plain region of the state, where the majority of hog farming operations are located. The on-site waste storage treatment lagoon is ~17,150 m^2, at the normal liquid level (~19,400 m^2 at the top of the bank) with a maximum liquid depth of 2.7 m and a maximum volume of ~42,080 m^3. The farm utilizes a conventional "lagoon and spray" technology as its primary means of handling effluent, which is the most widely used method in North Carolina. Effluent is flushed directly from the hog barns into the storage lagoon once per week and a portion of the stored lagoon wastewater is recycled to recharge the pit. Wastewater is also periodically removed and used as spray over on-site agricultural crops for nutrient enrichment purposes. Although effluent was flushed into the lagoon daily, the amount entering the system over a 1-week period was considered insignificant compared to the content of the entire lagoon and therefore, the additional effluent was not expected to affect measurements. Effluent was not flushed into the system near the experimental area. No mechanical mixing or stirring of the lagoon occurred during investigative periods.

2.2. *Dynamic flow-through chamber system and gas analyzers*

A flow-through dynamic chamber system with a variable-speed motor-driven continuous impeller stirrer (Aneja et al., 2000) was used to determine ammoniacal nitrogen (NH_3-N) and hydrogen sulfide (H_2S) flux from the lagoon. The dynamic chamber is a fluorinated ethylene propylene (FEP) Teflon-lined (2 mil thick, ~0.05 mm) open bottom cylinder (0.25 m internal diameter, 0.46 m internal height of chamber above water, and 25 L volume), inserted into a 0.61 × 0.61 m floatable platform. When placed over the lagoon, the chamber penetrated into the lagoon ~7 cm, effectively forming a seal between the lagoon surface and the air within the chamber. The chamber was randomly placed on the lagoon surface. A schematic of the chamber system is shown in Fig. 1.

Compressed zero-grade air (Machine and Welding Supply Company, Raleigh, NC) was used as a carrier gas and pumped through the chamber at a constant flow rate of ~9 L min^{-1}, controlled by a Model 810-S Mass Trak Flow Controller (Sierra Instruments, Monterey, CA). The air inside the chamber was ideally well mixed by a variable-speed motor-driven Teflon impeller stirrer ranging from speeds of 40 to 60 rpm for this study. Based on the impeller stirrer design, it is expected that the air flow characteristics inside the chamber at the air–water interface are similar to ambient air, i.e., flow outside the chamber, once steady-state has been reached (Perry and Chilton, 1973). The length of the Teflon tubing (0.40 cm inner diameter) connecting the chamber to the analyzers was < 10 m. The sample

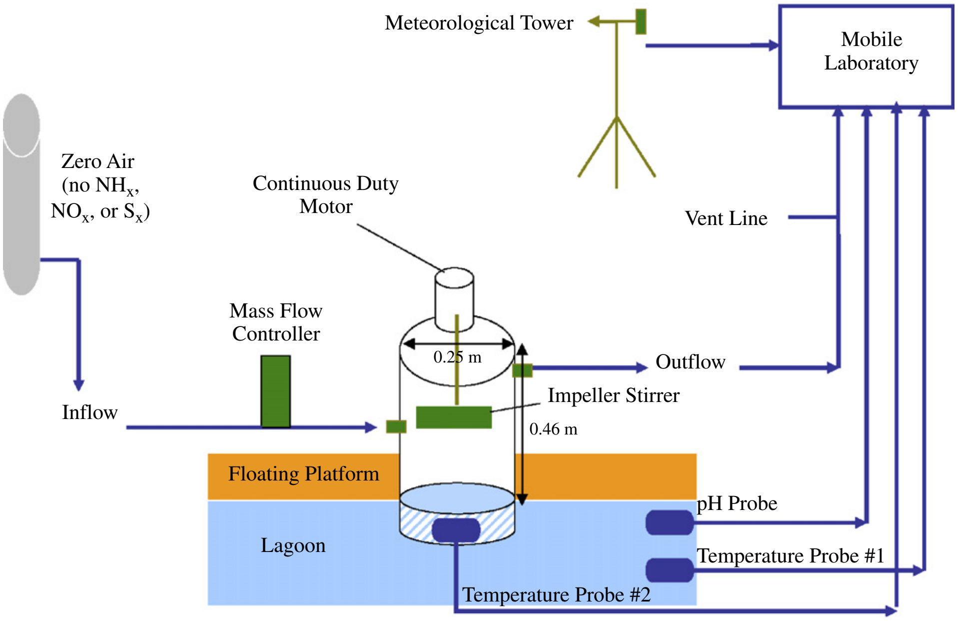

Fig. 1. Schematic of dynamic flow-through chamber system configured to measure emissions from a swine waste treatment lagoon.

exiting the chamber through the sample line was split in order to deliver the sample simultaneously to the different analysis instruments: a Model 450C pulsed fluorescence H_2S/SO_2 analyzer, and a Model 17C chemiluminescence NH_3 analyzer (Thermo Environmental Corporation, Mountain View, CA). Data collection was initiated once the chamber reached steady-state conditions (~30 min of operation). A vent line was fitted to the exiting sample line to prevent pressurization and was periodically bubble tested to check for under pressurization and/or leaks in the enclosed system.

Multi-point calibrations (80%, 60%, 40%, and 20% of full-range scale) for the Model 450C and Model 17C analyzers were conducted according to the TEI Model 450C and Model 17C instruction manuals prior to each sampling campaign using a TEI Model 146 dilution–titration system (Thermo Environmental Corporation, Mountain View, CA). Each instrument was zeroed and spanned daily during each measurement intensive.

2.3. Flux calculation

The mass balance for NH_3-N and H_2S in the chamber is given by

$$\frac{\mathrm{d}C}{\mathrm{d}t} = \left(\frac{Q[C]_\mathrm{o}}{V} + \frac{JA_\mathrm{L}}{V}\right) - \left(\frac{LA_\mathrm{C}[C]}{V} + \frac{Q[C]_\mathrm{f}}{V}\right) - R \tag{1}$$

where A_L is the lagoon surface area covered by the chamber, A_C is the inner surface area of the chamber, V is the volume of the chamber, Q is the flow rate of carrier gas through the chamber, J is the emission flux of the respective gas, $[C]$ is the gas concentration in the chamber, $[C]_\mathrm{f}$ is the gas concentration at the outlet of the chamber, L is the loss term by the chamber wall per unit area assumed first order in $[C]$, and R is the chemical production rate in the chamber.

Since compressed zero-grade air was used as the carrier gas, there is no inlet concentration of NH_3 or H_2S, $[C]_\mathrm{o} = 0$, and for a well-mixed chamber $[C]_\mathrm{f}$ may be assumed to be equal to the gas concentration everywhere in the chamber. The residence time in the chamber is relatively short (on the order of minutes) and therefore, no chemical reactions were expected to occur inside the chamber system ($R = 0$). Finally, at steady state the above equation reduces to

$$J = [C]_\mathrm{f}\left(\frac{LA_\mathrm{C}}{V} + \frac{Q}{V}\right)h \tag{2}$$

where h is the height of the chamber measured from the lagoon surface. The value of the total loss term for ammonia was obtained by conducting surface loss experiments as proposed by Kaplan et al. (1988), who provide a detailed description of the experiment. Upon statistical analysis, for steady-state conditions in the lagoon (i.e., when the flux was not increasing or decreasing significantly with time) it was determined that the loss term for NH_3-N flux increased exponentially as ambient temperature (T, in °C) increases ($n = 5$, $r^2 = 0.79$). An equation based on a semi-logarithmic relationship was then used throughout the experiment to calculate the loss of NH_3-N to the internal chamber walls and was given by

$$L_{\mathrm{NH_3\text{-}N}} = 0.0355T - 2.5454\,\mathrm{m\,min^{-1}} \tag{3}$$

The loss term was not considered for H_2S flux because solubility is much lower and the gas did not exhibit loss to the internal chamber walls.

2.4. Meteorological and lagoon parameters instrumentation

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

A Model CSIM11 pH probe (Campbell Scientific, Inc., Logan, UT) was used to continuously monitor near-surface lagoon pH. The pH probe was periodically buffer tested to ensure accuracy, and calibration curves were established. Two CS107 (Campbell Scientific, Inc., Logan, UT) temperature probes simultaneously measured lagoon surface temperatures inside the chamber as well as 0.3 m outside the chamber. For all measured 15-min averaged data ($n = 2017$), average lagoon near-surface temperatures were 17.9 ± 6.5 and 18.0 ± 6.6 °C inside and outside of the chamber system, respectively, and the correlation between the two measurements was very strong ($r^2 = 0.998$). The pH and temperature probes were each submerged in the lagoon at a depth of ~6–7 cm beneath the surface.

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

2.5. Lagoon sample collection

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

3. Results and discussion

Continuous in situ emissions measurements were made for NH_3-N and H_2S for ~1 week during each season (fall: October 26–November 1, 2004; winter: February 14–19, 2005; spring: April 14–18, 2005; summer: June 14–18, 2005) for a 1-year period. Data were not collected during precipitation or other disturbed weather events.

3.1. Diurnal and seasonal flux

A total of 1231 (NH_3-N) and 1672 (H_2S) 15-min averaged concentration values were recorded during the four seasonal experiments. During all seasons, NH_3-N flux was 3–4 orders of magnitude greater than H_2S flux from the lagoon. The NH_3 analyzer was set to collect data at the highest concentration range, maximum value of 20,000 ppb (parts per billion). Approximately 23% of the data recorded were above the maximum detectable limit, all during the spring and summer initiatives. Only two 15-min averaged concentration values within the range (< 20,000 ppb) were recorded during the summer. Alternatively, more than 60% of the 15-min averaged H_2S concentration values were recorded below the minimum detectable limit (1 ppb) and were therefore considered to be negligible. We note that only data recorded within the range for NH_3-N were used to examine the relationship between flux and several physicochemical parameters. Data recorded below the minimum detectable limit on the H_2S analyzer were considered to be negligible.

Table 1 summarizes the NH_3-N and H_2S fluxes from the lagoon for each season and data were further averaged to demonstrate the daily hourly averaged flux patterns in Fig. 2a, b. Randomly selected data points provide error bars (one standard deviation) to show variability in the seasonal measurements. Data gaps in the graphs represent times during the experiment when zero/span checks were being performed on the analyzers and cylinders containing the compressed zero-air were changed. No maximum flux values are reported in Table 1 for the spring and summer study periods. The average daily flux was at least 2495 and 4294 $\mu g\,N\,m^{-2}\,min^{-1}$ during the spring and summer, respectively. The spring and summer NH_3-N emissions presented in Fig. 2a represent minimum flux values because the 15-min averaged concentrations exceeded the maximum detectable limit of the analyzer during 29% (spring) and 99% (summer) of the data collection during the experiment, respectively. The actual flux for both spring and summer is assumed to be higher, but the extent of the increase is unknown. These data are graphed in Fig. 2a, in order to illustrate the seasonal effect on NH_3-N emissions. The lowest

Table 1
Statistical summary table of average daily NH_3–N and H_2S fluxes for each season

Season	Mean[a] ($\mu g\,m^{-2}\,min^{-1}$)	Minimum ($\mu g\,m^{-2}\,min^{-1}$)	Maximum ($\mu g\,m^{-2}\,min^{-1}$)
NH_3-N flux			
Fall 2004	1634(505)	1110	3305
Winter 2005	1290(246)	867	2027
Spring 2005	>2495[b]	1565	NA
Summer 2005	>4294[c]	3864	NA
H_2S flux			
Fall 2004	0.3(0.1)	0.0	0.8
Winter 2005	~0.0(0.2)	0.0	1.2
Spring 2005	0.5(1.0)	0.1	7.1
Summer 2005	5.3(3.2)	0.8	13.3

NH_3–N flux = (14/17)NH_3 flux.

[a] Numbers in parenthesis represent one standard deviation.

[b] NH_3 concentration was above maximum range on the ammonia analyzer for 29% of 15-min averaged data; maximum and average flux values are unknown.

[c] NH_3 concentration was above maximum range on the ammonia analyzer for 99% of 15-min averaged data; maximum and average flux values are unknown.

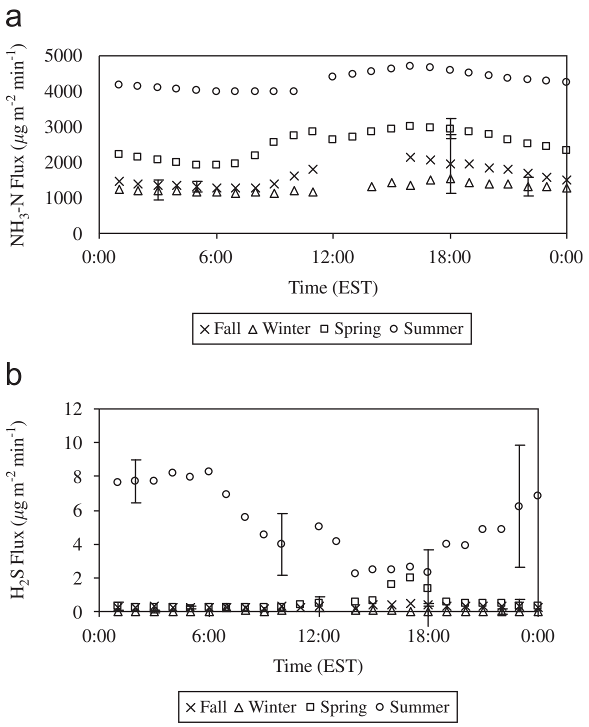

Fig. 2. Seasonally averaged diurnal variations of ammonia, NH_3-N (a) and hydrogen sulfide, H_2S (b) flux from anaerobic waste treatment storage lagoon. n (number of days averaged per season) = 6 in fall, $n = 5$ in winter, $n = 5$ in spring, and $n = 3$ and 5 for NH_3-N and H_2S, respectively, in summer. Vertical lines represent one standard deviation.

average daily fluxes for NH_3-N were observed during the fall and winter experimental period, 1634 and 1290 $\mu g\,N\,m^{-2}\,min^{-1}$, respectively. During these periods, a maximum was observed in the mid-to-late afternoon and a minimum was observed during the early morning.

Results of ammonia flux from previous studies are presented in Table 2. Flux estimates from all studies appear to be within one order of magnitude of each other. Higher pH values, lagoon TAN concentrations, and seasonal variations may account for some of the differences. Aneja et al. (2007) measured NH_3-N flux in 2002–2003 from the same lagoon used for this study. Results are comparable for the fall experiment; however, measured flux during the winter is ~3.5 times higher for this study. Zahn et al. (2001) report little variation from their three seasonal measurements with flux ranges of 1080–1104 $\mu g\,N\,m^{-2}\,min^{-1}$. Lim et al. (2003) reported a large variation in flux measurements at two different lagoons measured during the same season. The difference may be attributed in part to the lagoon size and manure input at each site. Previously, Aneja et al. (2000) reported a range of ammonia flux values of 305–4017 $\mu g\,N\,m^{-2}\,min^{-1}$ from another hog farm in North Carolina during four seasons and predicted the ammonia flux by an observational model

$$\log_{10}(NH_3\text{-N flux}) = 0.048T_L + 2.1,$$

where T_L is the near-surface lagoon temperature in °C.

Calculated NH_3-N emission factors are also presented in Table 2. Seasonal emission factors ranged from 12.4 kg NH_3-N $AU^{-1}\,yr^{-1}$ to more than 41.3 kg NH_3-N $AU^{-1}\,yr^{-1}$ (1 AU = 500 kg live animal weight). These estimates compare well with studies conducted by previous researchers (Aneja et al., 2000, 2007). The emission factors in this study are generally within a factor of 2 compared to other estimates made during the same time of the year.

During the winter season, only 2.3% of the H_2S concentration values were above the minimum detectable limit (1 ppb) for the analyzer and so the flux value was considered to be negligible. The highest observed average daily H_2S flux values, 5.3 $\mu g\,m^{-2}\,min^{-1}$, were observed during the summer. It is of interest to note the unusual diurnal flux pattern observed during this season. Hourly averaged flux values were highest during the nighttime and lowest during mid-afternoon. Yongsiri et al.

Table 2
Lagoon ammonia fluxes from previous studies compared with this study

Researcher	Season	Lagoon size (m^2)	Lagoon temperature (°C)	pH	TAN concentration ($mg\,L^{-1}$)	NH_3–N flux (μg $N\,m^{-2}\,min^{-1}$)	NH_3–N emission factors[a] ($kg\,N\,AU^{-1}\,yr^{-1}$)
Zahn et al. (2001)	August	7800	–	8.1	917±12	1080±36	
Zahn et al. (2001)	September	7800	–	8.2	934±8	1104±18	
Zahn et al. (2001)	October	7800	–	8.1	929±7	1104±24	
Lim et al. (2003)	April–July	30,735	25	8.1	2058	7264±1384	
Lim et al. (2003)	April–July	12,310	25	7.9	814	2718±1482	
Aneja et al. (2000)	August	~25,000	30	7.5	648±28[b]	4017±987	38.2
Aneja et al. (2000)	December	~25,000	12	8.0	663±34[b]	844±401	8.0
Aneja et al. (2000)	February	~25,000	12	7.8	642±39[b]	305±154	2.9
Aneja et al. (2000)	May	~25,000	25	7.7	603±48[b]	1706±552	16.2
Aneja et al. (2007)	September	15,170	27	8.1	442±18	2349±986	20.4
Aneja et al. (2007)	January	15,170	7	8.4	560±19	153±52	1.8
Aneja et al. (2007)[c]	October	17,150	25	8.2	364±36	1685±516	19.1
Aneja et al. (2007)[c]	January–February	17,150	7	8.1	636±37	370±147	4.3
This study	October–November	17,150	18	8.1	378±12	1634±505	15.7
This study	February	17,150	12	8.1	489±15	1290±246	12.4
This study	April	17,150	15	8.1	568±13	>2495	>24.0
This study	June	17,150	30	8.0	534±22	>4294	>41.3

[a] 1 AU = 500 kg live animal weight.
[b] Total Klejdahl nitrogen (TKN) reported.
[c] Same lagoon as this study (measured in 2002–2003).

(2004) report that at higher pH values (i.e., pH = 8) the increase in liquid temperature causes the molecular H_2S to dissociate to the ionic form bisulfide (HS^-). However, only molecular H_2S can transfer across the lagoon–air interface (the aqueous phase sulfide chemistry is described in greater detail in Section 3.2.2). Warmer temperatures are associated with increased biological lagoon activity (US EPA, 2002) and therefore the aqueous sulfide concentrations during summer are higher than other cooler seasons, likely accounting for the generally higher emissions. On the other hand, during the spring the flux maximizes during the mid-to-late afternoon although the values are much lower, $0.5\,\mu g\,m^{-2}\,min^{-1}$.

Results of hydrogen sulfide flux from previous studies are presented in Table 3. All data are from farms located in the Midwest US. The emissions reported are ~2–3 orders of magnitude greater than the results from this study, with the exception of Byler et al. (2004), who estimated average H_2S flux to be $4.2\,\mu g\,m^{-2}\,min^{-1}$ from three phototropic lagoons in eastern Nebraska during summer. Lim et al. (2003) reported considerably higher H_2S flux values of 546 and $136\,\mu g\,m^{-2}\,min^{-1}$ at two breed-to-wean farms in Illinois and Indiana during spring/summer. Neither study provided the time of day when the samples were collected and no data was reported for total dissolved sulfide concentrations in the lagoon. This parameter may account for the flux differences between the studies. Zahn et al. (2001) made continuous H_2S measurements during three separate measurement periods from August to October at a swine lagoon in eastern Missouri. Average flux ranged from $438\,\mu g\,m^{-2}\,min^{-1}$ in August to $1266\,\mu g\,m^{-2}\,min^{-1}$ in October. The lagoon sulfide content reported in the lagoon was considerably higher compared to this study.

Seasonal emission factors in this study were estimated to range between ~0 and ~0.5 kg $H_2S\,AU^{-1}\,yr^{-1}$, giving a mean annual emission factor of about 0.015 kg $H_2S\,AU^{-1}\,yr^{-1}$ (Table 3). To our knowledge, no other studies have reported H_2S emission factors from hog waste treatment lagoons.

3.2.1. *TAN and ammonia flux*

Ammonia (NH_3) and ammonium (NH_4^+) comprise TAN and only unionized NH_3 can transfer across the gas liquid interface. The TAN concentration values in the liquid manure (Table 4) were ~3–4 orders of magnitude larger than measured total dissolved sulfide and remained relatively constant during each

Table 3
Lagoon hydrogen sulfide fluxes from previous studies compared with this study

Researcher	Season	Experimental method	Lagoon size (m^2)	Lagoon temperature (°C)	pH	Sulfide	concentration ($mg\,L^{-1}$)	H_2S flux ($\mu g\,m^{-2}\,min^{-1}$)
H_2S emission factors[a] ($kg\,AU^{-1}\,yr^{-1}$)								
Zahn et al. (2001)	August	Theoretical shape profile	7800	–	8.1	15±2	438±24	
Zahn et al. (2001)	September	Theoretical shape profile	7800	–	8.2	17±3	492±24	
Zahn et al. (2001)	October	Theoretical shape profile	7800	–	8.1	18±1	1266±36	
Lim et al. (2003)	April–July	Tedlar bag collection via BCFC[b]	30735	25	8.1	–	546±96	
Lim et al. (2003)	April–July	Tedlar bag collection via BCFC[b]	12310	25	7.9	–	138±192	
Byler et al. (2004)[c]	May–June	Wind tunnel/Jerome meter		–	7.8	–	114[d]	
Byler et al. (2004)[c]	May–June	Wind tunnel/Jerome meter		–	7.4	–	192[e]	
Byler et al. (2004)[c]	July–August	Wind tunnel/Jerome meter		–	8.1	–	4.2[d]	
Byler et al. (2004)[c]	July–August	Wind tunnel/Jerome meter		–	7.7	–	19.2[e]	
This study	October–November	Dynamic flow-through chamber	17150	18	8.1	0.6±0.4	0.3±0.1	0.003
This study	February	Dynamic flow-through chamber	17150	12	8.1	3.2±3.3	~0.0	~0
This study	April	Dynamic flow-through chamber	17150	15	8.1	1.8±0.6	0.5±1.0	0.005
This study	June	Dynamic flow-through chamber	17150	30	8.0	9.2±2.5	5.3±3.2	0.051

[a] 1 AU = 500 kg live animal weight.

[b] Buoyant convective flux chamber.

[c] Average value from three lagoons.

[d] Measured from phototropic lagoon.

[e] Measured from non-phototropic lagoon.

experiment, ranging from seasonal averages of $378\,\text{mg N L}^{-1}$ in the fall to $568\,\text{mg N L}^{-1}$ in the spring. The amount of NH_3 that comprises TAN is dependent on lagoon temperature and pH and can be calculated based on work done by Emerson et al. (1975). The relationship between average daily NH_3-N flux and unionized NH_3 aqueous concentration (Fig. 3a) shows a linear increase ($r^2 = 0.82$). During this study, aqueous NH_3 was approximately 1–13% of measured TAN.

3.2.2. *Aqueous sulfide and hydrogen sulfide flux*

Aqueous H_2S exists in equilibrium with the bisulfide anion (HS^-) and the sulfide anion (S^{2-}) and all three comprise total dissolved sulfide (C_{TS}). Once total dissolved sulfide ($C_{TS} = H_2S + HS^- + S^{2-}$) concentration has been determined, the bulk dissolved hydrogen sulfide, which is a function of C_{TS}, pH, and lagoon temperature (T_L), can then be calculated. Snoeyink and Jenkins (1980) determined the relationship for the fraction of sulfide species (H_2S, HS^-, S^{2-}) present in aqueous solution as a function of pH (Fig. 4) and estimated the aqueous H_2S concentration for known C_{TS} by the following equation:

$$C_{H_2S} = C_{TS}\left(\frac{[H^+]^2}{[H^+]^2 + K_{a,1}[H^+] + K_{a,1}K_{a,2}}\right) \tag{4}$$

where C_{H_2S} is the concentration of dissolved hydrogen sulfide, $[H^+]$ is the hydrogen ion concentration (i.e., 10^{-pH}), and $K_{a,1}$ and $K_{a,2}$ are the acid

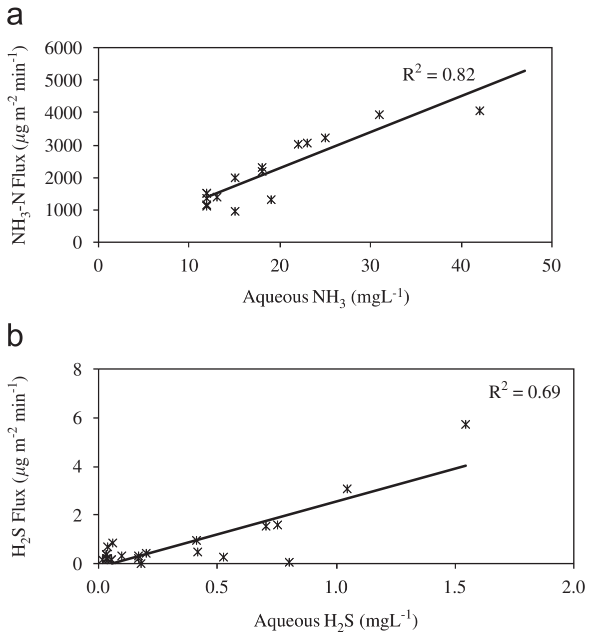

Fig. 3. (a) Average daily NH_3-N flux from lagoon surface plotted against aqueous NH_3 concentration sampled from lagoon on same day as measurements. (b) Average daily H_2S flux from lagoon surface plotted against aqueous H_2S concentration sampled from lagoon on same day as measurements.

Table 4
Sampling periods for NH_3–N and H_2S lagoon flux experiments and simple statistics (mean, standard deviation, and range) of effluent samples collected at least once per day and hourly averaged lagoon surface (~6–7 cm depth) parameters measured during the flux experiments

Season	Sample dates	TAN (mg L^{-1})	TKN-N (mg L^{-1})	Total dissolved sulfide (mg L^{-1})	Lagoon pH	Lagoon temperature (°C)
Fall	October 26–November 1, 2004	378(12)[a] 360–390[b] $n = 9$[c]	411(11) 400–430 $n = 9$	0.6(0.4) 0.3–1.5 $n = 9$	8.1 (~0.0) 8.0–8.2	18.2(1.7) 15.7–23.3
Winter	February 15–21, 2005	489(15) 470–510 $n = 8$	536(15) 520–560 $n = 8$	3.2(3.3) 0.1–9.4 $n = 8$	8.1 (~0.0) 8.0–8.2	11.5(1.4) 9.1–14.5
Spring	April 14–19, 2005	568(13) 550–590 $n = 6$	613(8) 600–620 $n = 6$	1.8(0.6) 1.0–2.5 $n = 6$	8.1 (~0.0) 8.0–8.2	15.1(1.7) 12.4–19.8
Summer	June 14–18, 2005	534(22) 520–570 $n = 5$	578(53) 540–650 $n = 5$	9.2(2.5) 6.4–13.0 $n = 5$	8.0 (0.1) 7.9–8.1	29.7(1.4) 26.9–32.5

[a] Mean value, number in parentheses represent one standard deviation.

[b] Range of measured values.

[c] n is the number of samples collected during each sampling initiative.

dissociation constants for H_2S and HS^-, respectively, in the aqueous phase.

The dissociation of molecular H_2S in water increases at pH values above 7 and conversely, as pH shifts from alkaline to acidic ($pH<7$), the potential for H_2S emissions increases. The sulfide anion can form at $pH>12$, well above the range for a typical hog lagoon, and so it is not expected to be present in the effluent sampled. Only the molecular $H_2S_{(aq)}$ fraction, not the ionized form (HS^-), can be transferred across the gas–liquid interface (US EPA, 1974).

Table 4 lists simple statistics for the aqueous sulfide concentrations measured during each season. Over the four seasons, measured concentrations ranged from 0.1 to 13.0 mg L^{-1}. The highest seasonally averaged total dissolved sulfide concentrations, 9.2 mg L^{-1}, were observed during the summer. Based on Eq. (4), the calculated average dissolved H_2S concentration generally comprised 10–17% of total dissolved sulfide, depending on pH and lagoon temperature. The relationship between average daily H_2S flux and lagoon H_2S aqueous concentration is illustrated in Fig. 3b and shows generally a linear increase ($r^2 = 0.69$). During the winter, both H_2S flux and aqueous concentration are low, likely due to low temperatures (average 11.5 °C) and subsequent low biological activity in the lagoon.

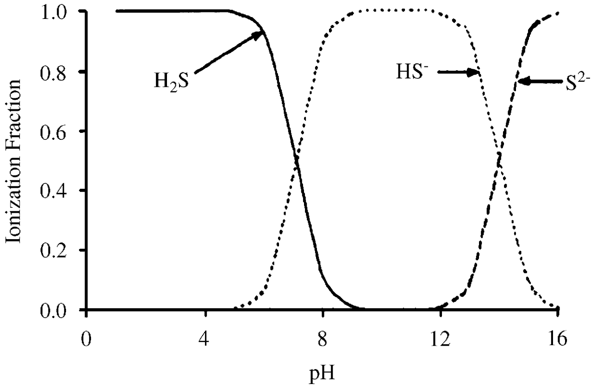

Fig. 4. Fractions of sulfide species (H_2S, HS^-, S^{2-}) present in aqueous solution as function of pH at 25 °C (*Source*: Snoeyink and Jenkins, 1980).

3.3. Lagoon pH and flux

Table 4 provides average pH values during the different seasonal measurement periods. The results show that there are only slight variations in pH throughout the year. The lowest seasonal average pH, 8.0 ± 0.1, was measured during the summer. Table 5 lists the Pearson correlation coefficient for the 15-min average NH_3-N and H_2S logarithmic flux values versus pH. For the logarithmic value of NH_3-N flux, results indicated that only ~4% of the variation could be explained by pH alone ($r^2 = 0.04$; $p<0.0001$). However, it is important to note that none of the flux values were considered for the correlation calculation when measured NH_3-N concentrations exceeded maximum values (20,000 ppb) on the analyzer. When the concentrations were above 20,000 ppb, the average lagoon pH was ~8.0, lower than the other three seasons (Fig. 5a). It is interesting to

Table 5

Pearson correlation coefficients for the log linear relationship between NH_3–N and H_2S flux, and some measured meteorological and lagoon parameters

Parameter	Pearson's correlation coefficient				
	pH	Lagoon temperature	Wind speed	Ambient temperature	Relative humidity
$\log_{10}$ NH_3–N flux ($n = 1050$)	−0.21 0.04 $p<0.0001$	0.51 0.26 $p<0.0001$	0.32 0.11 $p<0.0001$	0.38[a] 0.15[b] $p<0.0001$[c]	−0.58 0.34 $p<0.0001$
$\log_{10}$ H_2S flux ($n = 1386$)	−0.78 0.60 $p<0.0001$	0.83 0.69 $p<0.0001$	−0.14 0.02 $p<0.0001$	0.65 0.43 $p<0.0001$	0.03 ~0.0 $p = 0.22$

Each n represents a 15-min averaged value.

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

[b] Coefficient of determination (r^2): percent of variation that can be explained by the predictor variable.

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

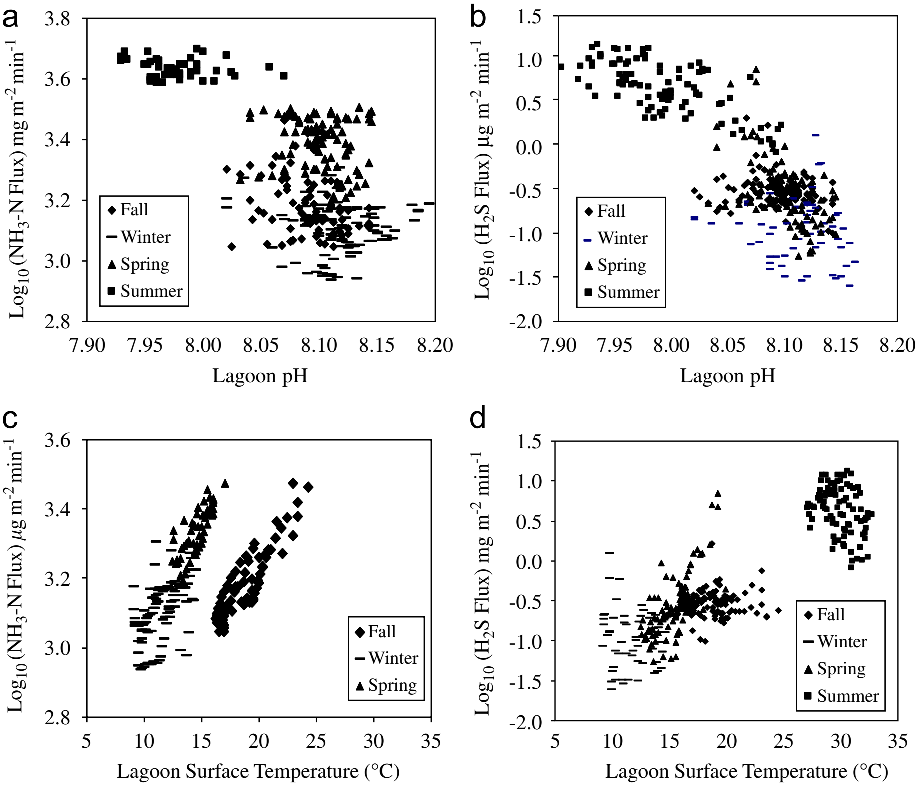

Fig. 5. Hourly averaged values for lagoon pH versus NH_3-N flux (a) and H_2S flux (b) and hourly averaged values for lagoon surface temperature versus NH_3-N flux (c) and H_2S flux (d). Only NH_3–N measured below detectable limits is provided for part (c).

notice that NH_3-N flux has a negative relationship with pH in this study. It would be expected that NH_3-N flux should increase as pH increases, indicating that other parameters combined (i.e., lagoon temperature and effluent concentration) may have a stronger influence. Also, the variation in pH during all four experiments may be considered small, ranging from 7.9 to 8.2 throughout the year.

The Pearson correlation coefficient ($r^2 = 0.60$; $p<0.0001$) for the 15-min averaged logarithmic H_2S flux value versus lagoon pH, indicates a negative relationship between H_2S flux and pH, as expected (Fig. 4). A semi-logarithmic plot of hourly averaged H_2S flux and pH further demonstrates the relationship (Fig. 5b).

3.4. Lagoon temperature and flux

The average lagoon temperature varied from 11.5 °C in the winter to 29.7 °C in the summer. For logarithmic NH_3-N flux, the correlation with lagoon temperature was strong ($p<0.0001$), with almost 26% (coefficient of determination, r^2) of the variability explained by lagoon temperature. Again, none of the flux values were considered when NH_3-N concentrations exceeded maximum values on the analyzer during measurements. At these high values, average lagoon temperatures were 24.9 °C. Fig. 5c provides a graph of the hourly averaged logarithmic NH_3-N values plotted against the respective lagoon temperatures. Values recorded above maximum detectable limits are not shown. The flux during the fall was considerably lower at the same lagoon temperatures as compared to the winter and spring experimental periods. However, it is important to recall that the aqueous TAN lagoon concentration was at least 100 mg L^{-1} lower during the fall as opposed to the other seasons. Unfortunately, for this study it was not possible to perform a multiple linear regression analysis including effluent concentration because lagoon samples were collected only once (or twice on occasion) per day as compared to all other parameters which are 15-min averaged continuous measurements.

The average lagoon temperature when H_2S was measured at concentration levels >1 ppb was

24.0 °C; while the average lagoon temperature was much lower (14.5 °C) when the concentration was considered negligible (<1 ppb). This is expected as anaerobic bacteria are ineffective at temperatures below 15 °C (US EPA, 2002). The Pearson correlation coefficient, r (Table 5) for the 15-min averaged logarithmic H_2S flux value and lagoon temperature was 0.83, $p<0.0001$, indicating that ~70% of the H_2S flux can be explained by the lagoon temperature. Fig. 5d shows the positive relationship between these two variables. However, as discussed previously, the lagoon temperature also affects the biological activity in the lagoon, and the higher activity likely leads to higher aqueous sulfide concentration levels.

3.5. *Meteorological parameters and flux*

Wind speed was measured at a reference height of 10 m. Utilizing the power law profile frequently used in air pollution applications (Arya, 1999), wind velocities (V) at 0.1 m (z, the height of the impeller stirrer in the chamber) were estimated. The power law profile is given by

$$\frac{V}{V_r} = \left(\frac{z}{z_r}\right)^m \quad (5)$$

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

NH_3-N emissions were positively correlated with ambient temperature and wind speed, $r^2 = 0.15$ and 0.11, respectively, while relative humidity was negatively correlated, $r^2 = 0.34$. All correlations were strong ($p<0.0001$); however, the relationship between each of the variables may be considered fairly weak.

Ambient temperature was positively correlated with logarithmic H_2S flux ($r^2 = 0.43$; $p<0.0001$) while wind speed showed a negative and much lower correlation ($r^2 = 0.02$; $p<0.0001$) (Table 5). Arogo et al. (1999) performed a laboratory study and determined a slight decrease in the H_2S mass transfer coefficient in aqueous solution as air velocity increased. Those results corroborated the observation by Whitman (1924) that wind speed above the surface will have a small effect on emissions of a relatively insoluble gas across the gas–liquid interface. There was essentially no statistically significant relationship for H_2S flux and relative humidity ($r^2 = \sim 0$; $p = 0.22$).

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

4. Conclusions

Emissions of atmospheric ammonia and hydrogen sulfide from a commercial anaerobic swine waste treatment lagoon were measured over a 1-year period during four different seasons in an effort to examine diurnal and seasonal variability and the respective relationships of NH_3-N and H_2S emissions to lagoon physicochemical properties and meteorological parameters. For NH_3-N, the largest fluxes were observed during the summer (>4200 μg N m^{-2} min^{-1}). During the fall and spring, average NH_3-N fluxes were 1634 ± 505 and >2495 μg N m^{-2} min^{-1}, respectively. The lowest fluxes were observed during the winter where average flux values were 1290 ± 246 μg N m^{-2} min^{-1}. The lowest fluxes for H_2S were also observed during the winter season and were considered to be negligible since concentration measurements were generally below the detection limit of the analysis instrument. Average fluxes increased during the fall (0.3 ± 0.1 μg m^{-2} min^{-1}) and spring (0.5 ± 1.0 μg m^{-2} min^{-1}) and were observed at highest flux values during the summer (5.3 ± 3.2 μg m^{-2} min^{-1}). Generally, the lagoon emissions for H_2S were ~3–4 orders of magnitude less than NH_3-N during all four measurement periods.

Hydrogen sulfide emissions were well correlated with lagoon aqueous H_2S concentration, lagoon temperature, and pH. Based on the dynamic-flow through chamber technique, ambient meteorological parameters, including wind speed and relative humidity, appeared to have much smaller influences over emission rates. Emissions of NH_3-N were influenced primarily by lagoon TAN measurements as well as lagoon temperature; however, in this study pH showed a slight negative correlation with NH_3-N flux.

The NH_3-N emission factors ranged from $\sim$10 to $\sim$40 $\mathrm{kg\,N\,AU^{-1}\,yr^{-1}}$. These estimates are well within the range of estimates by previous researchers and add to the growing database of agricultural ammonia emission factors.

This study also reports the first known seasonal emission factors for hydrogen sulfide flux from hog waste storage lagoons. Based on continuous measurements, emission factors ranged from $\sim$0 to $\sim$0.05 $\mathrm{kg\,H_2S\,AU^{-1}\,yr^{-1}}$, giving a mean annual emission factor of about 0.015 $\mathrm{kg\,H_2S\,AU^{-1}\,yr^{-1}}$.

Through complex photochemical reactions, the presence of ammonia and hydrogen sulfide in the atmosphere can lead to the formation of fine particulate matter (ammonium sulfate or ammonium bisulfate), which may have adverse environmental impacts on downwind areas and ecosystems. Quantifying these gaseous emissions will lead to more accurate modeling efforts to predict fine particulate formation in rural areas.

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