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ScienceDirect
Atmospheric Environment 40 (2006) S275–S286
ATMOSPHERIC ENVIRONMENT
www.elsevier.com/locate/atmosenv

Measurement and estimation of ammonia emissions from lagoon–atmosphere interface using a coupled mass transfer and chemical reactions model, and an equilibrium model

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Received 30 July 2005; received in revised form 31 October 2005; accepted 2 December 2005

Abstract

Ammonia has recently gained importance for its increasing atmospheric concentrations and its role in the formation of aerosols. The anaerobic lagoon and spray method, commonly used for waste storage and disposal in confined animal feeding operations (CAFO), is a significant source of ammonia emissions. An accurate emission model for ammonia from aqueous surfaces can help in the development of emission factors. Data collected from field measurements made at hog waste lagoons in south eastern North Carolina, using the flow through dynamic chamber technique, were used to evaluate the Coupled mass transfer and Chemical reactions model and Equilibrium model developed by Aneja et al. [2001a. Measurement and modeling of ammonia emissions at waste treatment lagoon-Atmospheric Interface. Water, Air and Soil pollution: Focus 1, 177–188]. Sensitivity analysis shows that ammonia flux increases exponentially with lagoon temperature and pH, but a linear increase was observed with an increase in total ammoniacal nitrogen (TAN). Ammonia flux also shows a nonlinear increase with increasing wind speed. Observed ammonia fluxes were generally lower in the cold season than in the warm season when lagoon temperatures are higher. About 41% of the equilibrium model predictions and 43% of the Coupled model predictions are found to be within a factor of two of the observed fluxes. Several model performance statistics were used to evaluate the performance of the two models against the observed flux data. These indicate that the simpler Equilibrium model does as well as the Coupled model. The possible effects of the "artificial" environment within the chamber, which is different from that in the ambient atmospheric conditions above the open lagoon surface, on the measured fluxes are also recognized.

Keywords: Ammonia flux; Coupled model; Equilibrium model; Mass transfer; Two-film transfer model

1. Introduction

Ammonia is an important atmospheric pollutant that plays a key role in several air pollution problems. Ammonia in the gaseous form is closely linked to the presence of ammonium in the atmosphere, which in turn acts as a neutralizing agent in the atmosphere and also contributes to the regional acidification problem (Warneck, 1999). Ammonium salts remain a major component of inorganic atmospheric aerosols and thus NH_x (NH_x = ammonia + ammonium) plays a major role in the

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doi:10.1016/j.atmosenv.2005.12.076

physical and chemical processes of the atmospheric nitrogen cycle. Ammonia is gaining increasing importance as a principle source of atmospheric aerosols (Baek et al., 2004). Ammonia reacts with acidic atmospheric species, such as sulfuric acid, nitric acid and hydrochloric acid, to form ammonium aerosols namely ammonium bisulfate, ammonium sulfate, ammonium nitrate and ammonium chloride. Approximately 10% of the atmospheric NH_3 also reacts with hydroxyl radicals to form amide radicals (Finlayson-Pitts and Pitts, 2000; McCulloch et al., 1998).

Ammonia concentrations increased in the rural atmosphere over eastern North Carolina between 1982 and 1997(Aneja et al., 2001b). The number of commercial swine facilities in North Carolina has increased dramatically, with the state's hog population increasing from approximately 2.8 million in 1990 to 9.8 million in 1996 when a moratorium on new commercial hog farms was placed (NCDENR, 1999). Measurements made at National Atmospheric Deposition Program/National Trends Networks sites in south eastern North Carolina showed an increasing trend in the ammonium concentration in the precipitation from 1990 to 1997 (Walker et al., 2000). As a regional-scale example, an emissions inventory prepared by the European Environment Agency, covering 28 European countries, shows that over 92% of the more than 5.6 million metric tons of ammonia emitted was agricultural in origin. Of this ammonia, about 80% was associated with the decomposition of livestock manure and the rest with the volatilization of fertilizer-N (NCDENR, 1999). Seventy five percent of swine production systems in North America and northern Europe use anaerobic or liquid/slurry systems for waste holding, which are major sources of ammonia emissions (Safley et al., 1992).

Measurements of ammonia emissions from hog waste treatment lagoons (Aneja et al., 2000, 2001a) and from fertilized and unfertilized soils (Roelle , 2001) have been made and analyzed with respect to relevant environmental parameters, including lagoon or soil temperature, pH and total ammoniacal nitrogen (TAN). Harper et al. (2004) studied the ammonia emissions from hog lagoons using micrometeorological technique. Todd et al. (2001) used a network of open-path Fourier transform infrared (FTIR) optical ray method to measure ammonia emission rates from the hog lagoon.

Other investigations have developed and utilized theoretical models to study ammonia emissions from animal waste and soil. Koelliker and Minor (1973) developed a desorption model for ammonia emissions using the two-film theory. Liang et al. (2002) developed mathematical model to study ammonia emissions from swine waste lagoons. The overall mass transfer co-efficient in this model depends on wind velocity and temperature and was based on an old study (Halsam et al., 1924). This gives an emission of zero under calm conditions with no wind. Asman et al. (1998) reviewed the ammonia research, including process description and emission factors for ammonia emissions. Olsen and Sommer (1993) modeled ammonia emissions from stored slurry considering the effects of wind speed and surface cover. A model to predict ammonia volatilization from flooded soils using TAN, pH, temperature, floodwater depth and wind speed was developed by Jayaweera and Mikkelsen (1990). Another model to predict ammonia volatilization from manure pits in swine buildings was used by Zhang et al. (1994). De Visscher et al. (2002) developed a two-layer model to study emissions from an anaerobic lagoon. The model uses effluent concentration, water temperature, wind speed and effluent pH. Aneja et al. (2001a) developed a coupled mass transfer and chemical reactions model and an Equilibrium model (hereafter called the Coupled model and Equilibrium model) to simulate ammonia emissions from swine waste lagoons. These models are based on the two-film theory of molecular transfer of ammonia across the lagoon–air interface. But the Coupled model takes into account pseudo-first order reaction of ammonia with water and acidic species (H_2SO_4, HNO_3, HCl) in the atmosphere, while it incorporates the effect of lagoon temperature, pH, and TAN, air temperature, wind speed, and ambient ammonia concentration. This model shows exponential increase with lagoon temperature and pH and linear increase with wind speed and TAN.

In this study, we have made comparisons of measured ammonia emission fluxes from swine waste treatment lagoon systems and modeled ammonia fluxes using both the Coupled and Equilibrium models developed by Aneja et al. (2001a). Such a comparison of measured and modeled emission fluxes can be used to test and validate these models. The results of this study can be utilized to estimate emissions from a large number of farms and can help us to develop an ammonia budget of a region containing those farms.

2. Sampling and measurement

2.1. Sampling locations and periods

As a part of project Odor, Pathogens and Emissions of Nitrogen (OPEN) ammonia flux measurements were made at 11 swine farm operations in eastern North Carolina. The waste from the hog sheds was flushed out with recycled lagoon water and discharged back into the waste lagoon from the top, often with additional treatment using potential environmentally superior technologies (ESTs). Each farm was sampled during two selected periods, one representing the warm season and the other representing the cold season. The list of farms and the month for the sampling times are given in Tables 1(a) and (b). Each farm was sampled for 8–10 days in each season. Only the lagoon component of hog farm was investigated in this study. Few farms have two lagoons, which are identified as suffix *A* and *B* after the farm number. Mean of observed flux and other parameters for different seasons is given in Tables 1(a) and (b). Fifteen minutes averaged measurements were made for ammonia flux and environmental data. This data was then averaged to 1 h period for use in this study.

Table 1
Mean values of observed flux and other parameters during the warm season

Lagoon	Wind speed ($m\,s^{-1}$)	Lagoon temperature (°C)	Air temperature (°C)	TAN ($mg\,l^{-1}$)	pH	Observed flux ($\mu g\ NH_3\text{-}N\,m^{-2}\,min^{-1}$)	Time of sampling
(a) *Warm season*							
Farms							
1-A	1.2	17.9	9.1	528.5	8.0	1524.0	Apr. 2002
1-B	2.0	19.4	17.0	401.6	8.2	1271.6	Apr. 2002
2-A	1.4	29.8	24.5	38.0	7.6	146.2	June 2004
2-B	1.2	27.8	23.0	383.6	7.4	636.8	June 2004
3	0.7	22.8	15.2	418.0	7.5	826.2	Sept. 2003
4-A	2.7	23.0	20.0	362.0	7.7	257.2	Sept. 2003
4-B	0.7	22.0	20.5	229.7	8.2	1233.4	Sept. 2003
5-B	1.7	28.2	23.7	303.7	7.1	2491.3	June 2003
6-A	2.3	29.1	26.1	647.2	8.6	6688.4	June 2004
6-B	2.3	26.8	24.0	171.9	8.2	3458.9	June 2004
7-A	2.5	24.8	22.6	157.6	6.9	1133.0	June 2002
7-B	2.4	26.9	25.1	37.8	8.0	454.4	June 2002
8-B	2.8	23.0	13.8	217.0	8.1	1213.9	Apr. 2004
9	1.4	24.6	23.4	371.9	8.2	1526.4	Feb. 2003
10-A	2.6	22.9	21.7	1121.4	7.5	1480.4	June 2003
11	1.3	26.7	24.2	467.4	8.1	2034.8	Sept. 2002
All	1.82	24.9	21.7	353.2	7.8	1545.1	
(b) *Cold season*							
Farms							
1-A	1.7	14.8	10.1	333.7	8.6	464.5	Nov. 2002
2-A	3.8	15.6	11.8	279.5	7.7	484.7	Apr. 2004
2-B	5.0	16.3	13.3	603.0	7.7	712.8	Apr. 2004
4-A	1.3	10.4	3.9	564.9	8.4	451.4	Dec. 2003
4-B	2.6	7.1	5.0	191.9	8.7	153.2	Dec. 2003
5-A	3.2	19.0	15.3	343.8	8.2	1667.7	Apr. 2003
5-B	2.2	18.8	17.4	362.3	8.2	1622.9	Apr. 2003
7-A	2.2	6.8	4.1	208.4	8.4	288.7	Dec. 2002
7-B	2.7	6.3	1.2	53.3	9.1	148.0	Dec. 2002
8-A	2.4	7.4	6.8	671.1	8.0	385.2	Feb. 2004
9	2.1	5.0	4.7	637.2	8.1	265.0	Feb. 2003
10-A	2.9	13.1	11.4	677.2	7.5	476.6	March 2003
10-B	2.1	17.9	15.5	328.9	8.2	1079.9	March 2003
11	3.9	7.2	6.8	558.4	8.4	134.6	Jan. 2003
All	2.6	10.7	8.4	433.0	8.2	538.1	

2.2. Instrumentation and measurements

A flow through dynamic chamber system with a variable-speed continuous impeller was used to measure NH_3 emissions from lagoon surfaces (Aneja et al., 2000; Chauhan, 1999; Kim et al., 1994). The translucent plastic cylindrical chamber is 45.7 cm high and has a diameter of 25 cm (a volume of 24.34 L). The chamber was fitted into a circular hole cut in the center of a floating platform (1.2×1.2 m). The cylinder penetrated into the lagoon to a depth 7 cm below the surface. The inside surface of the chamber was lined with a 5mil fluorinated ethylene propylene (FEP) Teflon sheet. A variable speed motor driven Teflon impeller was used to continuously mix the air inside the chamber. A carrier gas of compressed zero-air travels into the chamber through 0.635 cm outer diameter Teflon lines at a known flow rate between 4 and 8 lpm set by a mass flow controller and monitored by a datalogger. The sample air from the chamber, containing ammonia emitted from the water surface, travels through 0.635 cm Teflon tubing to the detection instrument. This whole system is lined with Teflon or stainless steel fitting in order to minimize chemical reactions with the sample flow. There is some concern, however, about the artificial environment within the chamber which is different from the open atmospheric conditions, particularly mean winds and turbulence, over the lagoon surface. We tried to adjust the impeller speed with the ambient wind speed at the top of the chamber. But, it is not possible to exactly match the turbulence inside the chamber with ambient turbulence above the lagoon surface. The impeller speed was set between 20 and 40 rpm.

A Thermo Environmental Instrument Incorporated (TECO) Model 17C chemiluminescnce ammonia analyzer was used to monitor ammonia concentration during ammonia flux measurement periods. The sample streams entering the analyzer is divided into three paths. The first path mixes the sample with ozone, and all of the nitric oxide in the sample reacts with ozone and yields nitrogen dioxide. The second path passes through a molybdenum converter (325 °C), which converts all the reactive oxidized forms of nitrogen (NO_y) to nitric oxide. This sample then reacts with ozone to quantify the concentration of all oxides of nitrogen. Third sample line passes through stainless steel converter (750 °C) which converts all nitrogen oxides and ammonia into nitric oxide, which gives total nitrogen (N_T). The sample stream alternates between three flow paths. Ammonia concentration is calculated by the difference between total nitrogen and total oxides of nitrogen as

$$[NH_3] = [N_T] - [NO_y]. \quad (1)$$

Ammonia analyzers were located in our temperature controlled mobile laboratory, which is maintained to be within the operating range of the instruments.

A 10 m meteorological tower was erected at each site to measure wind speed and direction, temperature and relative humidity. A Met One Instruments Model 034B-L Windset was used to measure wind speed and direction at 10 m above the surface. Air temperature and relative humidity (RH) measurements were made at 2 m height with a model HMP45C temperature and relative humidity probe housed in a radiation shield.

A CSI Model 11-L50 Innovative Sensors pH probe continuously monitored lagoon pH and C107 temperature probes measured lagoon temperature simultaneously inside the chamber. These pH and temperature probes were submerged in the lagoon at depths of 15–20 cm. Lagoon water samples were collected daily from measurement sites and were analysed for Total Kjeldahl Nitrogen (TKN) using a digestion procedure, which converts all organic and reduced nitrogen in the lagoon samples to NH_4^+. The NH_4^+ concentration in the sample was then determined by colorometry.

A Campbell Scientific CR23X Datalogger (PC208W software) was used continuously to collect data from all the instruments. Measurements were made continuously over the measurement period and data were averaged over 15 min and recorded at 15-min intervals during the sampling period.

3. Mass transport models

Two process-based models were developed by Aneja et al. (2001a) to determine ammonia flux from a lagoon–air interface. The principle characteristic of these models are the two thin layers or films of air and liquid (Fig. 1) above and below the air–liquid interface for molecular exchanges between water and air, respectively (Whitman and Davis, 1923; Cussler, 1996). Each layer of thickness t_i (for liquid phase $t_i = t_L$ and for air $t_i = t_a$) extends from air–liquid interface to the well-mixed region of turbulent transfer in the interior of the lagoon and

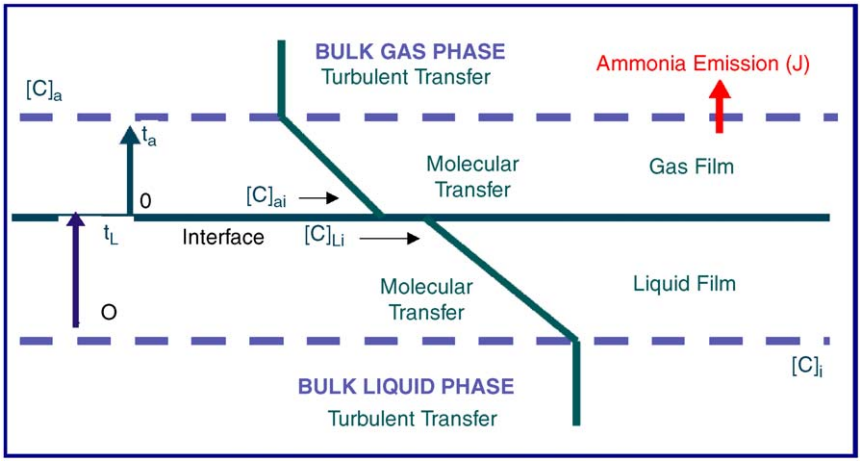

Fig. 1. Schematic of mass transfer across liquid and gas film.

atmosphere, respectively. All the resistance to mass transfer across the interface is due to the thin layer in which molecular transfer takes place.

3.1. Basic diffusion equation and its solutions

The steady state molecular diffusion equation for a horizontally homogenous thin layer in the liquid or gas (air) adjacent to the air–liquid interface is given by Arya (1999)

$$D_i \frac{d^2 C_i}{dz^2} = k_{ri} C_i, \tag{2}$$

where C_i is the concentration of the diffusing material, z is the vertical distance from the interface, D_i is the molecular diffusivity, and k_{ri} is the reaction constant for ammonia in the liquid or gas phases such that $D_i = D_L$ and $k_{ri} = k_{rL}$ for liquid and $D_i = D_a$ and $k_{ri} = k_{ra}$ for air, respectively. Liquid and gas phase reactions used in this study are further discussed in Sections 3.2 and 3.3.

Eq. (2) is a second-order differential equation, whose general solution is

$$C(z) = A \exp(r_i z) + B \exp(-r_i z), \tag{3}$$

where $r_i = \sqrt{k_{ri}/D_i}$ and the subscript i can be read as L for liquid and 'a' for air. Constant A and B can be evaluated using the following boundary conditions for the liquid and gas (air) films, respectively:

$$z = 0, \quad C_L(0) = C_L,$$
$$z = t_L, \quad C_L(t_L) = C_{Li}, \tag{4}$$

$$z = 0, \quad C_a(0) = C_{ai},$$
$$z = t_a, \quad C_a(t_a) = C_a. \tag{5}$$

Solution for the concentrations in liquid and air films can be derived as

$$C_{(z)} = \frac{C_{Li}(e^{r_L z} - e^{-r_L z}) - C_L(e^{(z-t_L)r_L} - e^{-(z-t_L)r_L})}{e^{r_L t_L} - e^{-r_L t_L}},$$
$$\text{for} \quad 0 < z \leqslant t_L, \tag{6}$$

$$C_{(z)} = \frac{C_a(e^{r_a z} - e^{-r_a z}) - C_{ai}(e^{(z-t_a)r_a} - e^{-(z-t_a)r_a})}{e^{r_a t_a} - e^{-r_a t_a}},$$
$$\text{for} \quad 0 < z \leqslant t_a. \tag{7}$$

In which C_{ai} and C_{Li} are related by the Henry's law constant as

$$C_{ai} = HC_{Li}. \tag{8}$$

Another condition to be satisfied by Eqs. (6) and (7) is that fluxes (J_i) at the interface in both the liquid and air film must be equal, i.e.

$$J_i = -D_L \left(\frac{dC}{dz}\right)_{z=t_L} = -D_a \left(\frac{dC}{dz}\right)_{z=0}. \tag{9}$$

Using the above condition, C_{Li} can be determined as

$$C_{Li} = \frac{2D_a C_a r_a (e^{r_L t_L} - e^{-r_L t_L}) + 2D_L C_L r_L (e^{r_a t_a} - e^{-r_a t_a})}{HD_a r_a (e^{r_a t_a} + e^{-r_a t_a})(e^{r_L t} - e^{-r_L t_L}) + D_L r_L (e^{r_a t_a} - e^{-r_a t_a})(e^{r_L t} + e^{-r_L t_L})}. \tag{10}$$

Therefore, the ammonia flux (J) at top of the air film is determined by the following relationship:

$$J = -D_a (dC/dz) \quad \text{at} \quad z = t_a. \tag{11}$$

Substituting from Eqs. (7) and (8) into Eq. (11),

$$J = D_a r_a \left[\frac{C_a(e^{r_a t_a} + e^{-r_a t_a}) - 2HC_{Li}}{e^{r_a t_a} - e^{-r_a t_a}}\right]. \quad (12)$$

In which C_{Li} is determined from Eq. (10).

3.2. Equilibrium model

Eq. (12) is an expression of ammonia flux considering chemical reactions of ammonia in both the liquid and air films. If we neglect chemical reactions in the two films, the above expression would reduce to a simpler form for an equilibrium model. For negligible reactions of ammonia in liquid and air films, reaction terms $r_a t_a$ and $r_L t_L$ will be very small and a Taylor series expansion can be applied for exponential terms in the above equation for the negligible chemical reactions. Thus, for the Equilibrium model, the ammonia flux is given by

$$J = -K(C_a - HC_L), \quad (13)$$

where $K = 1/(H/k_L + 1/k_a)$, is the overall mass transfer coefficient ($m\,s^{-1}$), k_L and k_a are the mass transfer coefficients for ammonia in liquid and air films, respectively, and H is the Henry's law coefficient. Mass transfer coefficients were used from Mackey and Yeon (1983), who calculated mass transfer coefficients as functions of wind speed (at 10 m height) in the form of friction velocity and Schmidt number for each phase. Henry's law coefficient was calculated as given by Hales and Drewes (1979).

3.3. Coupled mass transfer with chemical reactions model (Coupled model)

This model takes into account molecular diffusion and some chemical reactions. In the liquid film, only ammonia's reversible reaction in the water is considered, and pH is assumed constant. Using the following chemical reaction of ammonia in the liquid phase

$$NH_{3(aq)} + H_2O \rightarrow NH_4^+ + OH^-, \quad (14)$$

theoretical results of Olander (1960) can be used to determine the ammonia flux (J_i) in the liquid phase at the air–liquid interface

$$J = \frac{D_A}{t_L}(C_L - C_{Li})\left(1 + \frac{D_A}{D_c} \times K_L^*\right). \quad (15)$$

Here 'A' denotes ammonium (NH_4^+) and 'C' is ammonia (NH_3); D_A and D_C are the diffusivities of ammonium and ammonia in the liquid phase, respectively. C_L and C_{Li} are ammonia concentrations in the bulk of the liquid phase and at the interface, respectively, and $K_L^* = K_{NH_4^+}/[H^+]$, is a dimensionless parameter in which $K_{NH_4^+}$ is the equilibrium constant for the equilibrium equation of ammonium in the liquid, and $[H^+]$ is concentration of hydrogen ions calculated from pH.

Equilibrium constant is temperature dependant and was calculated from equation given by Jayaweera and Mikkelsen (1990).

From Eq. (9), at the liquid–air interface, fluxes are equal

$$J = \frac{D_A}{t_L}(C_L - C_{Li})\left(1 + \frac{D_C}{D_A} \times K_L^*\right) = -D_a\left[\frac{dC}{dz}\right]_{z=0} \text{ at } z = 0, \quad (16)$$

where C is the concentration in the air film as determined by Eq. (7).

Using Eqs. (7) and (8), ammonium concentration at the liquid–air interface is given by

$$C_{Li} = \frac{\frac{2D_a C_a r_a}{e^{r_a t_a} - e^{-r_a t_a}} + C_L \times \frac{D_A}{t_L} \times \left(1 + \frac{D_C}{D_A} \times K_L^*\right)}{HD_a r_a \times \left(\frac{e^{r_a t_a} + e^{-r_a t_a}}{e^{r_a t_a} - e^{-r_a t_a}}\right) + \frac{D_A}{t_L} \times \left(1 + \frac{D_C}{D_A} \times K_L^*\right)}. \quad (17)$$

The value of C_{Li} from Eq. (17) is used in Eq. (12) to calculate ammonia flux.

For the air film, the primary reactions of ammonia with sulfuric acid (H_2SO_4), nitric acid (HNO_3), hydrochloric acid (HCl), water, and the hydroxyl radical (OH) are considered (Finlayson-Pitts and Pitts, 2000; Warneck, 1999). In the air film, these five compounds are assumed to have constant concentrations, giving an effective first order reaction for ammonia, with first order reaction rate constant of ammonia in the gas phase, k_{ra}. Concentrations of these compounds were used from McCulloch et al. (1998).

4. Results and discussions

4.1. Sensitivity analysis of Equilibrium and Coupled models

The Coupled mass transfer and chemical reaction model and the Equilibrium model show strong dependence on lagoon temperature, lagoon pH, total

ammoniacal nitrogen (TAN) and wind speed. Aneja et al. (2001a) performed a sensitivity analysis of both the models with respect to physical and chemical parameters affecting ammonia flux. Lagoon temperature, pH, TAN, wind speed, air temperature, and ambient ammonia concentration were used to study their effects on ammonia flux. Lagoon temperature, pH, and TAN as well as wind speed were found to have significant effects on ammonia flux, while air temperature and ambient ammonia concentration did not show any significant effect on the ammonia flux for both the models. Model simulations show that as long as lagoon temperature remains constant, an increase of air temperature (T_{air}) from 5 to 40 °C yields a corresponding decrease in ammonia flux of less than 0.1% for both the models. This is mainly because the effect of atmospheric stability on the mass transfer coefficient is ignored in both the models. The variation in ambient ammonia concentration from 1 to 100 ppmv also gives flux changes of less than ~0.1%.

The modeled ammonia flux increases exponentially with the increase in lagoon temperature. Lagoon temperature affects the Henry's law coefficient, the liquid phase diffusivity of ammonia and ammonium, the dissociation constant, and viscosity and density of the liquid layer. The pH of a waste treatment lagoon controls the chemical equilibrium between ammonia and ammonium, and an increase in pH increases the fraction of ammonia in the solution. With an increase in pH, both models show an exponential increase in ammonia flux. Lagoon TAN controls the concentration of ammonia in lagoon water. Any increase in lagoon TAN gives a corresponding linear increase in ammonia flux. Since the air film is a laminar sub-layer, it is affected by meteorological and environmental parameters such as wind speed and stability. Thus wind speed may also affect ammonia emissions. Sensitivity analysis of both models show a polynomial (nonlinear) relationship between ammonia flux and wind speed.

4.2. Comparison of model predictions with observations

Ammonia flux and most of the lagoon and environmental data were averaged over 15 min intervals during the measurements periods for both the warm and cold seasons. But for the present analysis, those data were further averaged for 1 h periods. Although flux measurements were made for longer periods, only those hourly data are used for which all the required meteorological parameters (wind speed and air temperature) and lagoon parameters (lagoon pH, lagoon temperature and total ammoniacal nitrogen) were available. The numbers of hourly data used varied from lagoon to lagoon ranging from 11 to 160 h. The total number of hours of data used from all the lagoons in this study is 1574 h, which includes 706 h of data for the warm season and 868 h of data for the cold season.

Tables 1(a) and (b) give averages of wind speed, lagoon temperature, TAN, lagoon pH, air temperature, ammonia flux and measurement period for each lagoon during the warm and cold seasons, respectively. Average lagoon temperatures ranged from 5.0 to 19.0 °C in the cold season and from 17.9 to 29.8 °C in the warm season. Average wind speed ranged from 0.7 to 5 m s^{-1}. Average TAN ranged from as low as 37 mg l^{-1} to as high as 1121 mg l^{-1}. With a few exceptions, however, TAN mostly ranged between 300 and 600 mg l^{-1}. Average lagoon pH had a narrow range from 6.9 to 9.1. Average lagoon pH and TAN varied from lagoon to lagoon, but did not vary much during any given measurement period. Although air temperature varied a lot at each farm, it did not have any significant direct effect on ammonia flux as seen in our sensitivity studies. Of course, air temperature, in conjunction with other meteorological parameters, essentially determines the lagoon temperature which strongly affects the ammonia flux.

Observed ammonia fluxes were generally lower at low lagoon temperatures during the cold season than during the warm season with higher lagoon temperatures. This is because ammonia flux increases exponentially with increasing lagoon temperature. But there were a few exceptions (e.g., Farms 4-A and 2-A lagoons), when ammonia flux was higher during cold season than during the warm season. Higher values of lagoon pH, TAN and wind speed in cold season might explain these exceptions.

Lagoon temperature, pH, TAN, wind speed and air temperature are used as input to the Coupled and Equilibrium models to predict ammonia flux. Ambient ammonia concentration is also needed as an input to the Coupled and Equilibrium models. It was measured at 10 m height on a few farms only. As ambient ammonia does not have any significant effect on ammonia emission flux, an average value of 150 ppb was used for all calculations.

Models were run for both the warm season and cold season data. Each model's predicted fluxes were plotted against the hourly observed flux data

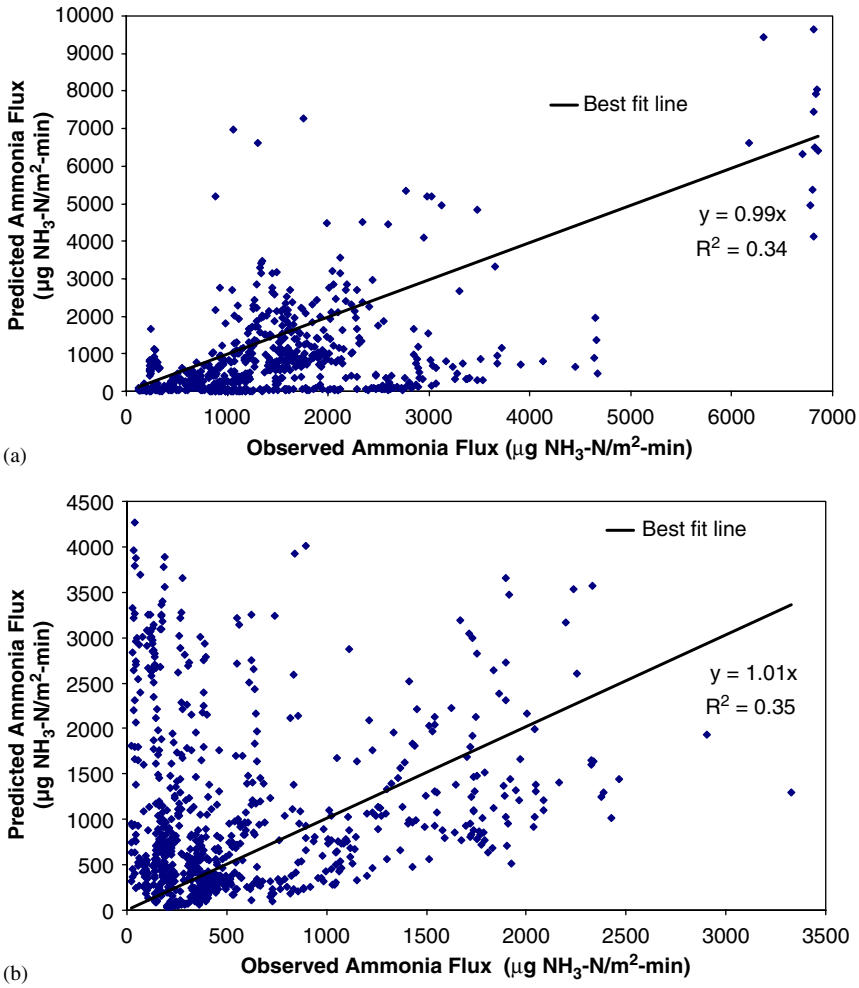

Fig. 2. (a) Comparison of Equilibrium model with observed ammonia flux data with a best fit line for warm season (Some high flux data points are out of the scale shown here). (b) Comparison of Equilibrium model with observed ammonia flux with best line in cold season.

from the dynamic flow through chamber system. Figs. 2–3 show these scatter plots of model predicted versus observed fluxes for both warm and cold seasons. A best fit line with X and Y representing the observed and modeled fluxes, respectively, is shown with the intercept set to zero, R^2 is also given for each plot.

Figs. 2(a) and (b) compare the observed flux with the Equilibrium model predictions during the warm and cold season, respectively. Correlations between the two were moderate with $R^2 = 0.34$ and 0.35, and slopes of the best-fitted line are 0.99 and 1.01 in warm and cold season, respectively. For the entire data set for both seasons (scatter plot not shown), $R^2 = 0.34$, and slope = 0.99. Figs. 3(a) and (b) compare the Coupled model predictions with observed ammonia fluxes with R^2 values of 0.35 and 0.45 and slopes of 1.96 and 1.61 for warm and cold season, respectively. For the combined data (scatter plot not shown), $R^2 = 0.36$ and slope = 1.90. Comparing the slopes of the best fitted lines with zero intercept for the two models, the Coupled model is found to significantly over-predict observed fluxes, while the Equilibrium model shows no significant bias.

Some of the predicted fluxes by both models were exceptionally high in the warm season when observed fluxes were higher than 5000 $\mu g\, NH_3\text{-}N\, m^{-2}\, min^{-1}$. These high ammonia fluxes could be due to the combined effect of high pH and lagoon temperature, as was observed at Harrells farm where average pH was 8.6 and average lagoon temperature was 29 °C. Ammonia flux increases exponentially with increase in pH or lagoon

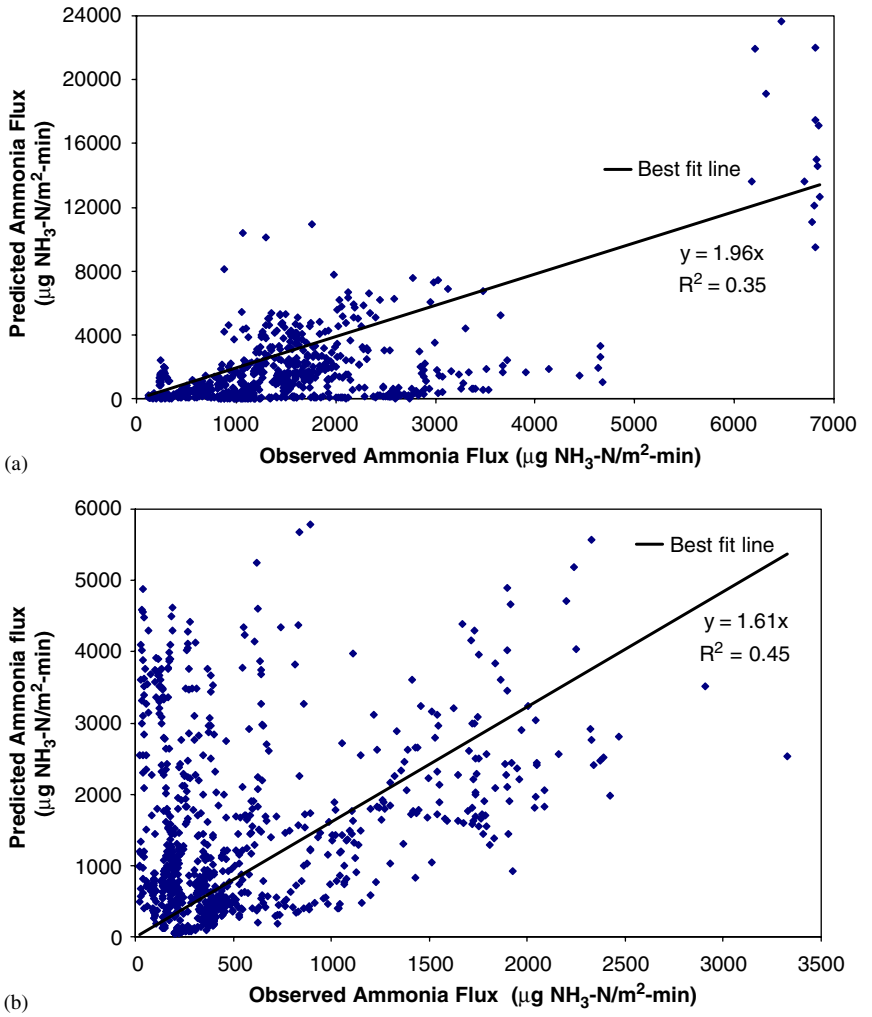

Fig. 3. (a) Comparison of Coupled model with observed ammonia flux data with best fit line for warm season (some high flux data points are out of the scale shown here). (b) Comparison of Coupled model with observed ammonia flux with best-fit line in cold season.

temperature. The scales of the *Y*-axis in Figs. 2(a) and 3(a) have been set to show the scatter of lower flux values, but the best fit lines take into account all the predicted values including the exceptionally high fluxes not shown in these plots.

Some of the predicted fluxes by both models in the warm season were exceptionally low as compared to observed fluxes. These low ammonia fluxes could be due to effect of low pH and low wind speed whose effects may not be fully and accurately accounted for in the two models.

4.3. Other model performance statistics

Various statistical measures have been proposed and utilized for evaluating the performance of air quality and dispersion models (see e.g. Irwin, 1983). Here, we have used a few simple statistical parameters, such as mean bias (MB), normalized mean bias (NMB), and normalized root-mean-square error (NRMSE), defined as

$$\mathrm{MB} = \overline{P} - \overline{O} = \frac{1}{N}\sum_{i=1}^{N}(P_i - O_i), \tag{18}$$

$$\mathrm{NMB} = (\overline{P} - \overline{O})/\overline{O}, \tag{19}$$

$$\mathrm{NRMSE} = \frac{1}{\overline{O}}\left[\frac{1}{N}\sum_{i=1}^{N}(P_i - O_i)^2\right]^{1/2}, \tag{20}$$

where $\overline{P}$ and $\overline{O}$ denote the overall mean predicted and observed fluxes, P_i and O_i are the predicted and

observed hourly fluxes, respectively, and N is the number of hourly observations. The above statistics were calculated for both the warm and cold seasons, separately, as well as for the combined data set.

Table 2 compares the mean flux, mean bias, normalized mean bias and normalized root-mean-square-error (NRMSE) for both the Equilibrium and Coupled models. Under warm conditions, observed mean flux lies between the predicted fluxes by the two models. Average predicted fluxes in the warm season are 1150.8 and 2210.8 $\mu g\,NH_3\text{-}N\,m^{-2}\,min^{-1}$ by the Equilibrium and Coupled models, respectively, whereas the observed flux was 1545.1 $\mu g\,NH_3\text{-}N\,m^{-2}\,min^{-1}$. The average bias in the Equilibrium model predictions is a negative with value of -394.3 $\mu g\,NH_3\text{-}N\,m^{-2}\,min^{-1}$, while the Coupled model predictions give an average bias of 665.7 $\mu g\,NH_3\text{-}N\,m^{-2}\,min^{-1}$. The corresponding values of NMB are −0.26 and 0.43. NRMSE in the Equilibrium and Coupled model predictions in the warm season are 1.76 and 3.58, respectively. In the cold season, mean predicted fluxes by the Equilibrium and Coupled models are 944.8 and 1391.3 $\mu g\,NH_3\text{-}N\,m^{-2}\,min^{-1}$, respectively, as compared to the mean observed flux of 538.1 $\mu g\,NH_3\text{-}N\,m^{-2}\,min^{-1}$. Both models are over predicting ammonia flux during the cold season with NMB values of 0.76 and 1.59 for the Equilibrium and Coupled models, respectively. Normalized mean bias in model predictions is higher in the cold season as compared to warm season. Predicted fluxes by the Equilibrium model gave NRMSE of 1.96 in cold season, while the Coupled model gave NRMSE of 2.69. The Equilibrium model gave higher NRMSE in the cold season while the Coupled model gave higher NRMSE in the warm season. For the combined data set, Equilibrium model predictions yielded $NMB = 0.05$ and $NRMSE = 2.01$, and Coupled model predictions gave $NMB = 0.78$ and $NRMSE = 3.90$. These model performance statistics indicate slight superiority of the simpler Equilibrium model over the more complicated Coupled mass transfer with chemical reactions model. Percentages of hourly model predicted fluxes that are within a factor of two of the observed hourly fluxes are comparable for the two models; these are less than 45%. We have examined separately the cases of gross over and under predictions (by more than a factor of 5) by the Equilibrium model.

Data points in Equilibrium model predictions where predictions were greater than observed ammonia flux by the factor of five or lower than the observed ammonia flux by the factor of five were selected. There were 166 out of 868 such over predictions in the cold season while 200 out of 706 such under predictions in the warm season. Lagoon and meteorological parameters for these data points were averaged and compared to seasonal averages of these parameters. In the warm season, TAN and pH averages, corresponding to these under predictions, were lower than the seasonal averages. TAN average was 234.4 $mg\,l^{-1}$ as compared to the warm season average of 353.2 $mg\,l^{-1}$ while pH was 7.1 as compared seasonal average of 7.8. The Equilibrium model predicts very low ammonia flux at low pH as ammonia flux shows an exponential increase with pH. This under prediction by the Equilibrium model

Table 2
Statistical performance parameters for equilibrium and coupled models

Statistical parameter	Equilibrium model prediction			Coupled model prediction			Observed		
	Warm season	Cold season	Combined data	Warm season	Cold season	Combined data	Warm season	Cold season	Combined data
Number of hours (N)	706	868	1574	706	868	1574	706	868	1574
Mean flux ($\mu g\,NH_3\text{-}N\,m^{-2}\,min^{-1}$)	1150.8	944.8	1037.2	2210.8	1391.3	1758.9	1545.1	538.1	989.7
Mean bias ($\mu g\,NH_3\text{-}N\,m^{-2}\,min^{-1}$)	−394.3	406.8	47.5	665.7	853.3	769.1	—	—	—
Normalized mean bias	−0.26	0.76	0.05	0.43	1.59	0.78	—	—	—
NRMSE	1.76	1.96	2.01	3.58	2.69	3.90	—	—	—
Percentage within a factor of 2	38	43	41	45	41	43	—	—	—

in the warm season may be because of low pH. In the cold season, wind speed and pH averages for these data points were higher than seasonal averages, while lagoon temperature and TAN averages were comparable. Wind speed was $4.5\,m\,s^{-1}$ as compared to cold season average of $2.6\,m\,s^{-1}$, while pH was 8.5 as compared to cold season average of 8.2. Ammonia flux in the Equilibrium model shows polynomial (non-linear) increase with increase in wind speed. This high wind speed and pH could be the reason for this over prediction in the cold season. It is possible that pH and wind speed effects may not be fully and accurately accounted for in the model. A more likely cause for the discrepancy in measured and modeled fluxes is the limited range of the impeller speed used for flux chamber measurements. Measured fluxes might be subjected to larger errors under both the strong and light wind conditions, so that model would apparently "overpredict" compared to the chamber-measured fluxes when winds were strong, and "underpredict" when winds were weak.

5. Conclusions

Ammonia flux measurements were made on swine waste treatment lagoons using a dynamic flow through chamber system. Hourly averages of wind speed, lagoon temperature, TAN, lagoon pH and air temperature were used as inputs into the two thin-film mass transfer models to predict ammonia flux and these predictions were compared with hourly averaged values of measured ammonia flux. Measurements made in the warm and cold season were analyzed and modeled separately to look into the seasonal differences between measured and predicted ammonia fluxes. Measured ammonia fluxes were higher in the warm season as compared to the cold season as high lagoon temperatures in the warm season lead to increased ammonia fluxes.

Both the Equilibrium model and the Coupled mass transfer with chemical reactions model predicted ammonia flux reasonably well in both seasons. Observed ammonia flux falls between predicted fluxes by the Equilibrium and Coupled models in the warm season, while both models overpredicted ammonia flux in the cold season. The Coupled model gave higher R^2 values in the both seasons, although the difference in R^2 of two models is small during the warm season. Slopes of best fit lines with zero intercept are 0.99 and 1.90 for the Equilibrium and Coupled models, respectively, indicating significant overprediction by the latter. Equilibrium model predictions gave lower value of NRMSE and bias than the Coupled model predictions in both seasons. Average of predicted fluxes by both models were within a factor of two of observed fluxes in both the warm and cold season, except by the Coupled model in the cold season when the mean was more than twice the observed flux. Considering all the hourly-averaged measurements and predictions, about 41% and 43% of the predictions by the Equilibrium and Coupled models, respectively, are found to be within a factor of two of the observations. Equilibrium model gave more consistent results as R^2, NRMSE and bias varied less between both seasons as compared to the Coupled model results. Our assessment of the performance of the two models against the measured flux using the dynamic chamber technique should be qualified by possible measurement errors and uncertainties due to the "artificial" environment within the chamber which is different from the ambient atmospheric conditions above the open lagoon surface. The limited range of impeller speed used, in particular, might cause larger errors in the measured fluxes under both strong and light-wind conditions.

Acknowledgements

Financial support provided by the North Carolina Animal and Poultry Waste Management Center is greatly appreciated. We sincerely acknowledge the help and support provided by Dr. Mike Williams and Ms. Lynn Worley-Davis. We thank the technology PIs, farm owners, Cavanaugh & Associates, and Mr. Bundy Lane, C. Stokes, and P. Moore for their cooperation. We acknowledge the discussions and gracious help provided by Dr. John Fountain, Dr. Richard Patty, Dr. Ray Fornes, and Dr. Johnny Wynne of North Carolina State University. We thank Mark Barnes, Guillermo Rameriz, and Rachael Huie. We also thank Mr. Hoke Kimball, Mr. Mark Yurka, and Mr. Wade Daniels all of NC Division of Air Quality for their support. Financial Support does not constitute an endorsement by the A&PWMC of the views expressed in the manuscript, nor does mention of trade names of commercial or noncommercial products constitute endorsement or recommendation for use.

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