An Empirical Model of Ammonium Ion Dissociation in Liquid Dairy Manure

V. K. Vaddella, P. M. Ndegwa, A. Jiang

ABSTRACT. *Emission of ammonia (NH_3) from lagoons or other similar animal manure holding structures not only degrades environmental quality but also lowers the fertilizer value of the liquid effluent. In general, NH_3 emissions from these facilities depend on the concentration of free NH_3 in the liquid ($NH_{3(aq)}$), which is a function of the dissociation of ammonium ions (NH_4^+). The dissociation of NH_4^+ is dependent on manure properties, including temperature, pH, ionic strength, and total suspended solids (TSS) concentration. The dissociation constant of NH_4^+ (K_d) in flushed dairy manure was determined at a pH of 9, temperatures of 5°C, 15°C, 25°C, and 35°C, and total solids (TS) contents of 0.5%, 1.0%, 1.5%, 2.0%, and 2.5% w/w, and a regression model was obtained. The K_d value increased by approximately 1.6× for every 10°C rise in temperature. The data also indicated a logarithmic decay in K_d with an increase in the concentration of TS in the liquid. The coefficient of determination (R^2) of 0.97 for the nonlinear empirical model of K_d as a function of both temperature and TS concentration demonstrated good fit to the experimental data. The K_d values in the dairy manure with 1.5% TS were 117%, 87%, 61%, and 54% compared to the theoretical K_d values in pure water-ammonium solutions at 5°, 15°, 25°, and 35°C, respectively. Similar trends were observed at other TS concentrations, suggesting that the effects of solids were more significant at elevated temperatures. The results of this study emphasize the need for including both the TS concentration and the temperature in models of K_d for liquid dairy manure, in addition to ensuring that the entire ranges of TS and temperature encountered in the region where the model will be used are covered.*

Keywords. Ammonia emission, Ammonium dissociation, Connective emission chamber (CEC), Dairy manure, Modeling.

In liquid dairy manure, nitrogen (N) exists both in inorganic and organic forms. Total ammoniacal nitrogen (TAN), which is inorganic in nature, is the sum of ionized ammonium N (NH_4^+-N) and un-ionized ammonia N (NH_3-N). In general, only the latter (NH_3-N) nitrogen species can directly volatilize from dairy wastewater into the atmosphere. In theory, therefore, increased NH_3-N in manure increases the potential of air pollution from animal feeding operations (Sommer et al., 2005; Ni, 1999). In addition to potential air pollution, emission of NH_3 also reduces the fertilizer value of the dairy lagoon effluent when it is eventually applied on crop fields or pastures (Sørensen and Amato, 2002).

Several methods exist for quantifying the TAN concentration in aqueous solutions (APHA, 1998). In general, however, there is no direct method for measuring the proportion of TAN that is NH_3-N in aqueous solutions. In aqueous ammonium solutions, NH_3, NH_4^+, and hydrogen ions (H^+) exist in equilibrium, which is usually represented by equation 1 (Sommer et al., 2005):

$$[NH_4^+] \overset{K_d}{\Leftrightarrow} [NH_3] + [H^+] \qquad (1)$$
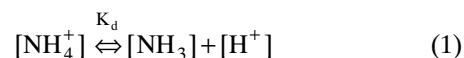
This equilibrium is dependent on both the liquid temperature and pH. Lowering the liquid pH shifts the equilibrium to the left, thus lowering the concentration of NH_3-N in the liquid. This is the basic theory behind acidification of manure slurries to mitigate emissions of NH_3 or to prevent loss of NH_3 during storage of manure samples in order to preserve their integrity.

The value of K_d is mainly a function of the liquid temperature and the pH of the liquid manure. The variation of free NH_3-N concentration relative to TAN with the temperature and pH of the aqueous solution, adopted from Loehr (1984), is presented in figure 1. It is evident that with an increase in temperature, the fraction of NH_3-N concentration increases. It is also clear that with an increase in pH, the fraction of NH_3-N to TAN (denoted as α) increases and approaches 1.0 at pH values higher than 11. This scenario suggests that if the liquid pH is greater than 11, then total volatilization of TAN as NH_3 gas into the air is theoretically possible. This concept will be explored later in the Methods and Materials section to develop a procedure for determination of K_d in the laboratory. The K_d value in dilute aqueous solutions at 25°C is presented in equation 2. Based on the Clausius-Clapeyron equation, Jayaweera and Mikkelsen (1990) proposed equation 3 to calculate K_d values in pure water-ammonium solutions as a function of temperature. Alternative equations for

The authors are **Venkata K. Vaddella,** Post-Doctoral Fellow, Department of Animal Sciences and Biosystems Engineering, Michigan State University, East Lansing, Michigan; **Pius M. Ndegwa, ASABE Member,** Associate Professor, Department of Biological Systems Engineering, Washington State University, Pullman, Washington; and **Anping Jiang,** Executive Deputy Director and Chief Engineer, Sound Global, Ltd., RM15-02 Sound Group, Majuqiao, Tongzhou District, Beijing, China. **Corresponding author:** Pius M. Ndegwa, Department of Biological Systems Engineering, Washington State University, P.O. Box 646120, Pullman, WA 99164; phone: 509-335-8167; e-mail: ndegwa@wsu.edu.
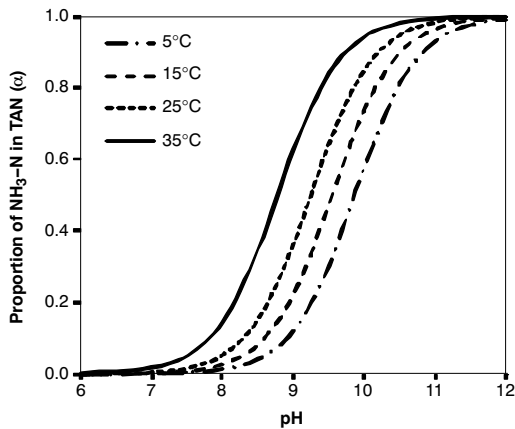
Figure 1. Proportion of total ammoniacal nitrogen that is ammonia (α) as a function of temperature and pH in aqueous solutions.

computing K_d in pure water-ammonium solutions were proposed by Emerson et al. (1975) based on empirical NH_4^+ ionization constants (eq. 4). More recently, Montes et al. (2009) developed equation 5 from basic thermodynamic principles.

$$K_d = \frac{[NH_3]_{aq}[H^+]}{[NH_4^+]} \equiv 5.62 \times 10^{-10} \qquad (2)$$

$$K_d = 10^{-[0.0897 + (2729)/T]} \qquad (3)$$

$$K_d = 10^{-[0.09018 + (2729.92)/T]} \qquad (4)$$

$$K_d = 10^{[0.05(2788)/T]} \qquad (5)$$

In general, because equations 2, 3, 4, and 5 were developed for pure water-ammonia solutions, they are also valid for dilute aqueous solutions where the activity coefficients of the ions are approximately one. In concentrated solutions, however, it is important to account for ionic strength effects on the chemical activity of the ions, which result in a reduction of the K_d value (Arogo et al. 2003; Clegg and Whitfield, 1995; Snoeyink and Jenkins, 1980). Bell et al. (2007) incorporated the effect of ionic strength on K_d in saline water solutions by multiplying the activity coefficient of each ion ($\gamma\{i\}$) with the concentration of the ion in question, as shown in equation 6. The ionic activity coefficients are calculated from either the classical Debye-Hückel equation for dilute solutions or the extended Debye-Hückel equation for more concentrated solutions, using the ionic strength (μ) of the solution. Snoeyink and Jenkins (1980) suggested equations 7 and 8 for approximating μ using total dissolved solids (TDS) and electrical conductivity (EC), respectively:

$$K_d = \frac{\gamma\{NH_3\}[NH_3]_{aq}\gamma\{H^+\}[H^+]}{\gamma\{NH_4^+\}[NH_4^+]} \qquad (6)$$

$$\mu = TDS(2.5 \times 10^{-5}) \qquad (7)$$

$$\mu = EC(1.6 \times 10^{-5}) \qquad (8)$$

A few studies have reported the effect of TS concentrations on the K_d value in livestock manures. The K_d in swine

manure with 0.25% TS and 400 mg L^{-1} TAN at 25°C was about 52% of the K_d for deionized (DI) water (Liang et al., 2002). The K_d in 1% TS swine manure was about 20% of the K_d in pure water (Zhang, 1992). The K_d in chicken manure with 3.5% to 8.5% TS was about 16.7% of the K_d in pure water solution (Hashimoto and Ludington, 1971). In 0.3% TS swine manure, Arogo et al. (2003) obtained empirical K_d values of 0.94, 0.5, and 0.51 of the K_d in pure water at 15°C, 25°C, and 35°C, respectively. Lower K_d values in livestock manures compared to pure water-ammonium solutions have been attributed to higher solution ionic strength caused by the dissolved solutes, as well as adsorption of TAN on organic matter, which results in reduced chemical activity of NH_3 and NH_4^+ (Liang et al., 2002; De Visscher et al., 2002; Zhang, 1992; Snoeyink and Jenkins, 1980). To our knowledge, no studies exist in the available literature on the effect of TS on K_d in dairy manure. The K_d value is a critical component of process models for estimating NH_3 emissions, and such data would allow more accurate representation of K_d. Effectively, this would result in enhanced models for determining NH_3 emissions from dairy wastewaters, which is crucial not only for regulatory purposes but also for development of NH_3 emission mitigating strategies from dairy manure.

The objectives of this study were to determine, through controlled laboratory studies, the effects of temperature and TS concentration on the K_d value in liquid dairy manure and obtain an empirical model that represents these effects.

METHODS AND MATERIALS

PROCEDURE FOR DETERMINING AMMONIUM DISSOCIATION CONSTANT

There is no standard procedure or method to directly determine NH_3-N in aqueous solutions (Arogo et al., 2003; Emerson et al., 1975). However, determination of TAN (the sum of NH_3-N and NH_4^+-N) is a standard protocol in most wastewater analyses. At a given pH, K_d can be calculated from equation 9 if the fraction of NH_3-N in the TAN (denoted as α or $[NH_3]/([NH_3] + [NH_4^+])$ is known and by noting that $[NH_4^+]/[NH_3] = [H^+]/K_d$ and that pH = $-\log_{10}[H^+]$:

$$K_d = \frac{\alpha}{1-\alpha} 10^{-pH} \qquad (9)$$

To compute K_d using equation 9, the main challenge is determining the value of α at the corresponding pH value. This requires knowing the NH_3-N component, which cannot be determined directly as mentioned earlier. The procedure for determining α at a particular pH described by Arogo et al. (2003) was adapted in this study. Equation 10 has been used by several authors (Liang et al., 2002; Arogo et al., 1999; Zhang, 1992; Hashimoto and Ludington, 1971) to model NH_3 volatilization from liquid into air:

$$\frac{dM_{TAN}}{dt} = h_m A \left([NH_3]_L - [NH_3]_{air}\right) \qquad (10)$$

where M_{TAN} is the mass of total NH_3-N and NH_4^+-N (kg) in the given bulk liquid with surface area A (m^2), h_m is the overall mass transfer coefficient (m s^{-1}), and $[NH_3]_L$, and $[NH_3]_{air}$ are the concentrations of NH_3 in liquid and air, respectively (g L^{-1}). This equation is further simplified to equation 11 by noting that, in comparison to the concentration of NH_3 in liq-

uid ($[NH_3]_L$), the concentration of NH_3 in air ($[NH_3]_{air}$) is negligible:

$$\frac{d\mathrm{M}_{\mathrm{TAN}}}{dt} = -h_m A[NH_3]_L \tag{11}$$

The negative sign in equation 11 is an indication that the concentration will decrease over time, and equation 11 can be further simplified to equation 12 by noting that $\mathrm{M}_{\mathrm{TAN}} = V \times \mathrm{TAN}$ (V is the volume of liquid manure) and substituting $\alpha\mathrm{TAN}$ for $[NH_3]_L$:

$$\frac{d(\mathrm{TAN})}{d\mathrm{T}} = -h_m\alpha\frac{A}{V}(\mathrm{TAN}) \tag{12}$$

Equation 13 is obtained by integrating equation 12 between 0 and time t, and between initial TAN (TAN_0) and residual TAN at time t (TAN_t). Equation 14, a more convenient transformation of equation 13, was the basis for experimental determination of α from measurements of residual TAN with t in a convective emission chamber (CEC). A plot of $\ln(\mathrm{TAN}_t/\mathrm{TAN}_0)$ against time t yields a straight line with a slope (s), as given in equation 15:

$$\mathrm{TAN}_t = \mathrm{TAN}_0 e^{-\left(h_m\alpha\frac{A}{V}\right)t} \tag{13}$$

$$\ln\left[\frac{\mathrm{TAN}_t}{\mathrm{TAN}_0}\right] = -h_m\frac{A}{V}\alpha t \tag{14}$$

$$s = -h_m\frac{A}{V}\alpha \tag{15}$$

The fraction of TAN present as NH_3 (α) will approach 1.0 at a pH above 11. This is the basic premise in the experimental determination of α (and hence K_d) at different pH values. To determine α at any other pH of interest (α_{int}), the change in TAN with t must be studied at the pH of interest and also at another pH where α is close to 1 (in this case, any pH above 11 will do). The respective slopes are determined at the two conditions to yield equations 16 and 17, respectively. Dividing equation 16 by equation 17 provides the value for α_{int} as shown in equation 18. This procedure is repeated within the entire range of conditions of interest to generate data for developing an empirical model of K_d as a function of T and TS:

$$S_{\mathrm{pH(int)}} = -h_m\frac{A}{V}\alpha_{\mathrm{pH(int)}} \tag{16}$$

$$S_{\mathrm{pH}\geq 11} = -h_m\frac{A}{V}(1) \tag{17}$$

$$\alpha_{\mathrm{pH(int)}} = \frac{S_{\mathrm{pH(int)}}}{S_{\mathrm{pH}\geq 11}} \tag{18}$$

EQUIPMENT AND INSTRUMENTATION USED IN THIS STUDY

This study was achieved through a series of experiments conducted in a convective emissions chamber (CEC). The CEC consisted of a wind generator, an airflow controller unit, an air heater and temperature control unit, two screens (3 mm stainless steel, 120 cm apart) to effect turbulence, and a liquid manure sample chamber, which included a temperature-
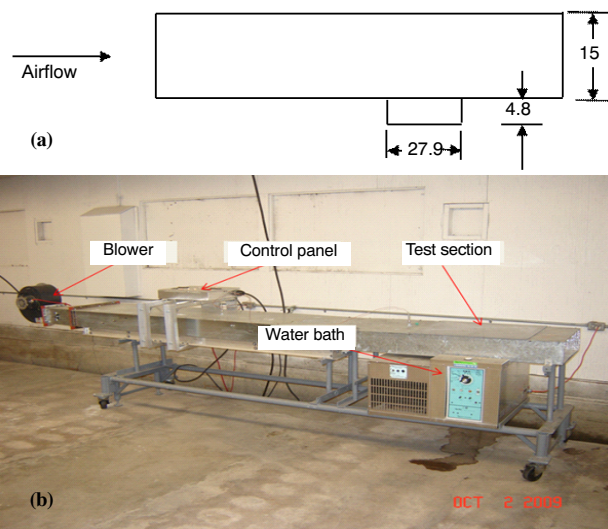

Figure 2. Convective emission chamber (CEC): (a) cross-section of the test section of the CEC (dimensions in cm but not to scale), and (b) photograph of the CEC.

controlled water bath and a manure sample pan. The CEC was replicated from previous similar studies (Arogo et al., 1999; Shaw, 1994; Zhang, 1992). The dimensions of the test section of the CEC are presented in figure 2a, and figure 2b is a photograph of the CEC. The overall dimensions of the CEC were 4.2 m × 0.45 m × 0.15 m (L ×W ×H). The CEC walls were built with galvanized-iron sheet and insulated from inside to avoid any heat transfer with the surroundings. The liquid manure sample pan (27.9 cm × 17.5 cm × 4.8 cm) was placed in a constant-temperature water bath to maintain a constant manure temperature throughout each experimental run. The water bath and air heaters maintained constant temperature within ±1°C of the desired manure and air temperatures.

EXPERIMENTAL PLAN

The manure used in this study was collected from the equalization tank in the Washington State University Dairy Research Facility in one batch and stored in a walk-in cooler in the lab. The manure collection system in this facility consists of manure scraping into pits, from which the manure is then flushed using supernatant water drawn from the secondary lagoon. The flushed manure is taken through a solids-liquid separator, and the liquid portion is delivered into the equalization tank. The manure is finally pumped from the equalization tank into the primary lagoon, which overflows into the secondary lagoon. Appropriate manure samples were drawn from this batch prior to running each experiment. The TS concentrations were adjusted with tap water to range from 0.5% to 2.5% (at increments of 0.5%), which represents typical dairy flush manure. The liquid manure temperatures were set between 5°C and 35°C at increments of 10°C. Each experimental run was conducted with a 2.3 L sample of test liquid manure with pH adjusted to 9.0 (pH of interest) or 12 using 10 M NaOH.

The pH-adjusted manure sample was poured into the test pan and placed in the constant-temperature water bath. Spot checking of the temperature of the manure sample ensured that the desired set temperature remained constant during an entire test. A constant airflow velocity of 1.5 m s⁻¹ was main-

Table 1. Experimental plan for studying ammonium dissociation in liquid-dairy manure.

| Run	Solids Content (%)	Liquid Temperature (°C)
1	0.5	25
2	1.0	25
3	1.5	25
4	2.0	25
5	2.5	25
6	1.5	5
7	1.5	15
8	1.5	35

tained at 1.0 cm above the test liquid. Before placing the manure pan in the temperature-controlled water bath, the CEC was operated for at least 20 min to stabilize to the test conditions. Once the test conditions were achieved, the manure pan was placed in the water bath, and the CEC was run for approximately 30 min to allow the manure liquid to adjust to the test conditions. Once the manure liquid had adjusted to the test conditions, five samples of 1 mL each were drawn from approximately 2 mm below the liquid surface, using a 5 mL pipette, and combined into a composite sample every 30 min for 3 h. The five sample locations were randomly selected but were spread over the entire surface of the test manure. To avoid NH_3 loss, these manure samples were injected, directly from the pipette, into 5 mL of 2 M sulfuric acid. In most cases, the samples were analyzed immediately after the experiment using a standard method (EPA Method 350.2). Three sets of runs (i.e., triplicate runs) were conducted at a pH of 9 and at a pH of 12. The pH values of the test manure samples were determined at the beginning and end of each test run. The experiment plan is outlined in the table 1.

DATA ANALYSIS

Regression analyses were performed to analyze the effects of manure temperature (5°C, 15°C, 25°C, and 35°C) and TS concentration (0.5%, 1.0%, 1.5%, 2.0%, and 2.5% w/w) on K_d. The model of K_d was obtained using Proc NLIN (SAS, 2006) with the entire data set for the environmental and liquid manure conditions examined in this study. Proc NLIN is the SAS procedure for fitting nonlinear regression models. The justification for using Proc NLIN is provided in the Results and Discussion section.

RESULTS AND DISCUSSION

Two examples of the exponential decay profiles of TAN in the dairy manure liquid from the start to the end of test runs (at 25°C and 1.5% TS) are given in figure 3. The TAN residuals in the dairy manure liquid with time at a pH of 9 are shown in figure 3a, while figure 3b represents the TAN residuals in the dairy manure liquid with time at a pH of 12. With reference to equation 18, two test conditions are required to obtain α of interest, which is necessary for computing the K_d at the pH of interest (pH_{int}). The TAN residual curves evidently followed first-order kinetics very well, with R^2 values of 0.95 at pH 9 and 0.99 at pH 12. The slope obtained from figure 3a with a pH of 9 was 9.26×10^{-4}, and the slope obtained from figure 3b with a pH of 12 (α = 1) was 3.56×10^{-3}. Dividing the slope obtained from figure 3a with the slope obtained from figure 3b resulted in an α value of 0.26. This value represents the fraction of TAN that is NH_3-N in the dairy
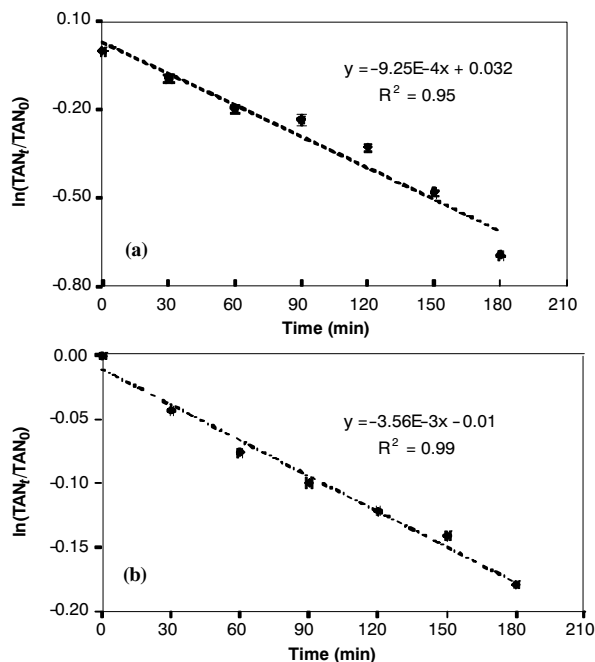
Figure 3. Plots of the natural logarithms of the ratio of residual TAN to initial TAN in the dairy manure liquid at 25°C and 1.5% TS and at (a) pH 9 and (b) pH 12 with time (error bars indicate standard deviations from means).

manure liquid with 1.5% TS, maintained at 25°C, at a pH of 9, and with an air velocity of 1.5 m s^{-1}. The computed K_d obtained with these parameters was 3.51×10^{-10}. Similar computations were done to determine the K_d values at all other test conditions examined in this study.

EFFECT OF TEMPERATURE ON DISSOCIATION CONSTANT

The effect of temperature on K_d in 1.5% TS liquid dairy manure is shown in figure 4a. The K_d in liquid dairy manure increased exponentially ($R^2 = 1.00$) with an increase in temperature for the range of temperatures investigated in this study. The effect of temperature on K_d was further analyzed using the classical van't Hoff model shown in equation 19 (Silbey et al., 2005):

$$\ln[K] = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (19)$$

where K is the equilibrium constant, ΔH is the change in enthalpy (J mole[-1]), ΔS is the change in entropy (J mole[-1]), R is the universal gas constant (8.314 J mole[-1] K^{-1}), and T is the temperature (K). In general, the van't Hoff model provides a physical relationship between K_d and temperature for dissociating chemical compounds. A graphical presentation of the van't Hoff equation fitted using the K_d and temperature data obtained from this study is presented in figure 4b. It is clear that the effect of temperature on the K_d in dairy manure can be presented by a simple van't Hoff model, given the strong correlation coefficient (R^2) of 0.99. The equation generated in figure 4b can thus be used to correct K_d for temperature or for prediction of K_d values within the temperature range investigated in our study.

For comparison, the K_d values in liquid dairy manure at temperatures ranging between 5°C and 35°C, TS concentration of 1.5%, and at a pH of 9 obtained from our

Figure 5. Plots of theoretical and experimental K_d values of NH_4^+ from current study (for 1.5% TS dairy manure) and previous studies (table 1).
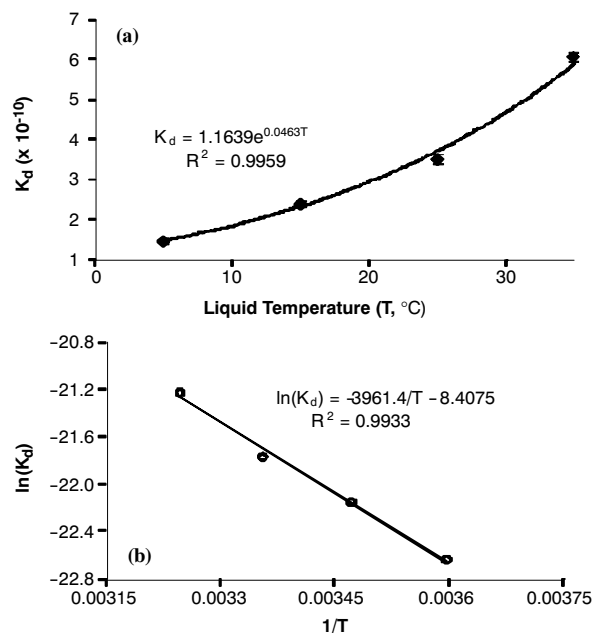
Figure 4. (a) Graphical presentation of dissociation constant of ammonium as a function of temperature, and (b) linear regression fit of the van't Hoff model based on the same data.

study and the K_d values reported in the literature are presented in figure 5. Details of the source of these K_d values, their method of derivation, and medium in which they are valid are summarized in table 2. Based on figure 5, it is evident that there were no significant differences between the results obtained from the Emerson et al. (1975) model compared to the results obtained from the Jayaweera and Mikkelsen (1990) model. However, the values obtained with the Montes et al. (2009) model were lower than those from the former two theoretical models. It is also quite apparent that irrespective of the TS concentration, the K_d values in pure water, swine manure, and dairy manure demonstrate similar trends: the K_d in all cases increased with the increase in temperature.

The computed K_d in pure water increased by approximately 2× for every 10°C rise in temperature (2.2× between 5°C and 15°C, 2.1× between 15°C and 25°C, and 2.0× between 25°C and 35°C), which is in conformity with the van't Hoff theory. However, the predicted K_d values from our model increased by approximately 1.6× for every 10°C rise in temperature. These results further demonstrate that our model predictions are in agreement with the predictions from theoretical models (Emerson et al., 1975; Jayaweera
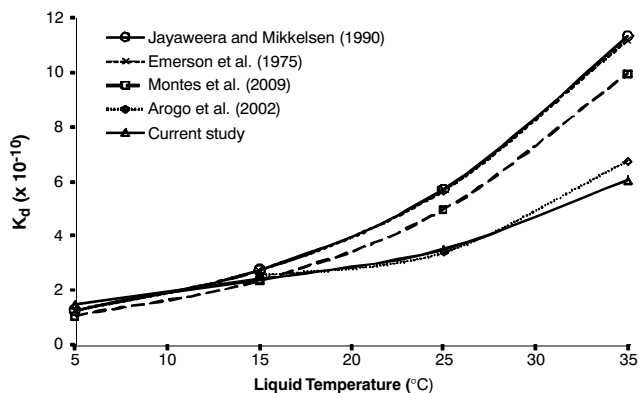
and Mikkelsen, 1990) when the effects of total solids (i.e., suspended solids and ionic strength) are taken into account. Inhibition of dissociation of NH_4^+ by the suspended solids and the higher ionic strength inherent in the dairy manure most probably explains the fact that the K_d in dairy manure did not double in accordance with the theoretical models, nor with the van't Hoff model, for every 10°C rise in temperature, which is exhibited in pure water.

EFFECT OF TS CONCENTRATIONS ON DISSOCIATION CONSTANT

A natural regression plot ($R^2 = 0.96$) showing the effect of TS concentrations on the K_d in liquid dairy manure at 25°C is presented in figure 6. The K_d in the liquid dairy manure decreased with an increase in the TS concentration. This result further demonstrates that the presence of solids in dairy manure inhibits dissociation of NH_4^+ and that the greater the TS concentration, the greater the inhibition. The observed reduced K_d in livestock manures has been explained in previous studies. In general, lower values of K_d in livestock manures compared to pure water-ammonium solutions have been attributed to higher solution ionic strength caused by the dissolved solutes as well as adsorption of TAN on organic matter, which results in reduced chemical activity of NH_3 and NH_4^+ (Montes et al., 2009; Arogo et al., 2003; Liang et al., 2002; De Visscher et al. 2002; Zhang 1992; Snoeyink and Jenkins, 1980).

Other researchers have related the K_d in liquid animal manures with the K_d in pure water via simple fractions. For example, Liang et al. (2002) noted that the K_d in swine manure with 0.25% TS and 400 mg L^{-1} TAN at 25°C was approximately 52% of the value in deionized (DI) water.

Table 2. Theoretical and experimental K_d values from current and previous studies.

| K_d Value	Applicable in	Derivation Method	Source
$K_d = 10^{-(2.0153 + 1.208 \times TS) \times [1.8944 + (819.8)/T]}$	0.5% to 2.5% TS and pH 9 dairy manure	Empirical studies	Current study
0.94, 0.5, and 0.51 of K_d in pure water at 15°C, 25°C, and 35°C	0.3% TS and pH 9 swine manure	Empirical studies	Arogo et al. (2003)
$K_d = 10^{-[0.0897 + (2729)/T]}$	Pure water-ammonium solutions	Basic thermodynamic principles (Clausius-Clapeyron equation)	Jayaweera and Mikkelsen (1990)
$K_d = 10^{-[0.09018 + (2729.92)/T]}$	Pure water-ammonium solutions	Empirical NH_4^+ ionization constants	Emerson et al. (1975)
$K_d = 10^{[0.05 + (2788)/T]}$	Pure water-ammonium solutions	Basic thermodynamic principles (van't Hoff equation)	Montes et al. (2009)
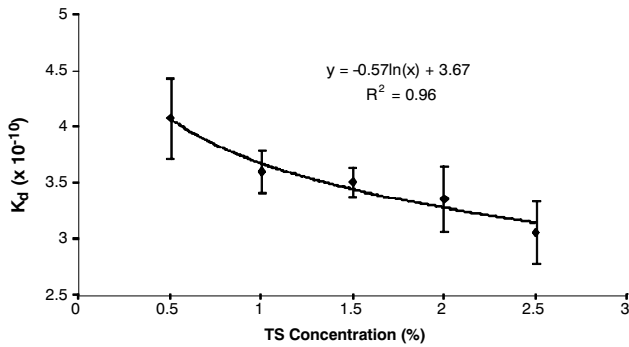
Figure 6. Effect of total solids (TS) concentrations on K_d values of NH_4^+ in liquid dairy manure (error bars indicate standard deviations from means).
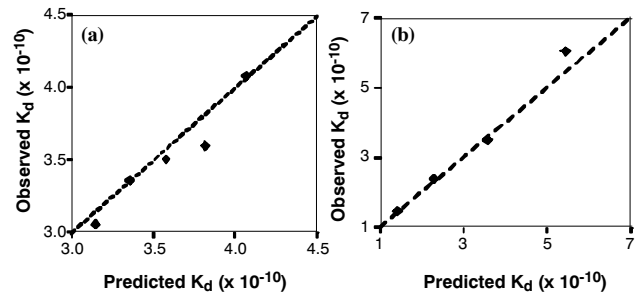

Figure 7. Observed versus predicted K_d values at (a) different temperatures and fixed TS of 1.5% and (b) different TS concentrations and fixed temperature of 25°C.

Zhang (1992) noted that the K_d in 1% TS swine manure was about 0.2 times (20%) the K_d in water. Hashimoto and Ludington (1971) reported that the K_d in chicken manure with 3.5% to 8.5% TS was about 1/6, or 16.7%, of the K_d in anhydrous NH_3 solution. There are no grounds to challenge the usefulness of these simple fractions, particularly for the specific conditions in which they were determined. However, based on our current study and that of Arogo et al. (2003), it is quite clear that such simplistic approaches to providing a single empirical fraction to represent the K_d in animal manures is not tenable over the entire range of interest of both the TS and temperature.

EFFECT OF T-TS INTERACTIONS ON DISSOCIATION CONSTANT

The K_d values in liquid dairy manure with 1.5% TS at 5°C, 15°C, 25°C, and 35°C were 1.17, 0.87, 0.61, and 0.54 times, respectively, the theoretical K_d values in pure water at similar temperature conditions estimated with either the Emerson et al. (1975) model or the Jayaweera and Mikkelsen (1990) model. This observation shows that, at constant TS concentration (1.5%), the ratios of K_d values in dairy manure to the K_d values in pure water decreased with an increase in the liquid temperatures. This observation further illustrates the significance of TS concentrations on the K_d values at elevated temperatures. We can also further postulate that because the effect of TS concentration increases with an increase in the manure temperature, there is interaction between temperature and TS concentration. The latter observation suggests that models of K_d in liquid dairy manure must consider the simultaneous effects of the TS concentration and the temperature. This observation is also reflected in the data obtained with dilute swine manure by Arogo et al. (2003).

MODEL OF AMMONIUM DISSOCIATION CONSTANT

To model K_d based on manure temperature (T), we adopted the general equation (eq. 20) developed for correcting K_d for temperature by various authors (Montes et al., 2009; Jayaweera and Mikkelsen, 1990; Emerson et al., 1975). In equation 20, we noted that K_d increases with an increase in temperature (A and B are constants), an observation that was also verified in the current study (fig. 4). On the other hand, the effect of TS concentration on K_d was incorporated into equation 21 by noting that K_d decreases with an increase in TS (where C and D are constants). This

conjecture was based on the data gathered in the current study (fig. 6) in conjunction with data from previous studies (Arogo et al., 1999; Zhang, 1992; Hashimoto and Ludington, 1971):

$$K_d = 10^{-(A+(B)/T)} \tag{20}$$

$$K_d = 10^{-(C+D\times TS)\times(A+(B)/T)} \tag{21}$$

The K_d values obtained at different TS concentrations at various manure temperatures were the input to Proc NLIN, the nonlinear regression procedure in SAS (2006). From the results of Proc NLIN, the respective constants were obtained, resulting in the empirical model presented in equation 22, whose R^2 value of 0.97 ($n = 24$) indicated a good fit to the experimental data:
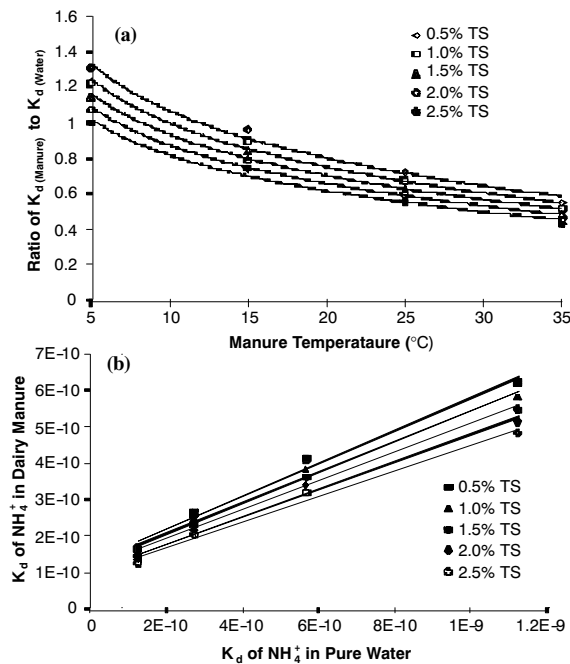
$$K_d = 10^{-(2.0153+1.208\times TS)\times(1.8944+(819.8)/T)} \tag{22}$$

where TS = total solids concentration (w/w; 0.5% means TS = 0.005), and T = temperature (K). The expected relationships between K_d and TS concentration and T are evident, i.e., decreasing K_d with increase in TS and increasing K_d with increase in T, demonstrating the physical soundness of the model.

A comparison of observed values and model-predicted values of K_d at different temperatures (5°C, 15°C, 25°C, and 35°C) at the TS concentration of 1.5%, for example, is shown in figure 7a. In addition, a comparison between observed values and model-predicted values of K_d at different TS concentrations (0.5%, 1.0%, 1.5%, and 2.5%) at 25°C is presented in figure 7b. In both cases, the observed values compared very well with the model-predicted values, further illustrating the good fit of the nonlinear regression model to the experimental data.

EXPANDED UTILITY OF OUR MODEL

The expanded utility of our model is quite apparent from the graphical format (fig. 8) of the relationships between our model and the models developed for pure water-ammonium solutions, in this case the Emerson et al. (1975) model. The ratio of the K_d in liquid dairy manure and the K_d in pure water within the ranges of manure conditions (5°C to 35°C and 0.5% to 2.5% TS) examined in this study are presented in figure 8a. On the other hand, the K_d in liquid dairy manure as a function of the K_d in pure water within the same conditions is presented in figure 8b. Two important aspects are explicit in figure 8: (1) the concentration of TS is a significant factor governing the K_d in dairy manure, and

(a)

Ratio of $K_{d\,(Manure)}$ to $K_{d\,(Water)}$

1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0

◇ 0.5% TS
□ 1.0% TS
▲ 1.5% TS
◓ 2.0% TS
◕ 2.5% TS

5   10   15   20   25   30   35

Manure Temperataure (°C)

(b)

K_d of NH_4^+ in Dairy Manure

7E-10
6E-10
5E-10
4E-10
3E-10
2E-10
1E-10
0

■ 0.5% TS
▲ 1.0% TS
■ 1.5% TS
◆ 2.0% TS
◓ 2.5% TS

0   2E-10   4E-10   6E-10   8E-10   1E-9   1.2E-9

K_d of NH_4^+ in Pure Water

Figure 8. Graphical presentations of (a) ratio of the dissociation of ammonia in dairy manure to its theoretical dissociation in pure water as a function of temperature, and (b) dissociation of ammonia in dairy manure in relation to its dissociation in pure water.

(2) the effect of TS on K_d becomes more significant at elevated temperatures. Given the strong statistical relationships (all $R^2 = 0.99$) exhibited in figure 8, these curves can be interpolated to provide accurate values for the K_d in liquid dairy manure at any manure condition within the conditions (5°C to 35°C, and 0.5% to 2.5% TS) covered in our study. Although our study was focused on manure conditions normally experienced in the Pacific Northwest of the U.S., these conditions are common in many other regions. The results of our study are, therefore, applicable in many other regions. Furthermore, we are of the opinion that this study can be extended as desired to cover a much broader range of conditions, to expand the utility of such models globally.

SUMMARY AND CONCLUSIONS

A series of laboratory experiments was conducted in a convective emissions chamber to model K_d at temperatures between 5°C and 35°C and at TS concentrations ranging from 0.5% to 2.5%. The conclusions drawn from this study are as follows:

- When the effect of temperature was considered alone, the K_d in dairy manure increased with an increase in temperature. From 5°C to 35°C, the K_d increased by approximately 1.6× for every 10°C rise in temperature. The K_d temperature dependence in the manure was described using a simple van't Hoff model. These findings indicate that an increase in temperature results in a greater fraction of un-ionized NH_3-N, which can in turn result in increased NH_3 emissions into the surroundings. This conclusion is in line with theoretical expectations.

- The K_d decreased at a decreasing rate (logarithmic decay) with an increase in the TS concentration in the manure, suggesting reduced NH_4^+ dissociation with increasing TS level in liquid dairy manure.

- The empirical model (eq. 22) developed for K_d as a function of temperature and TS concentration had an R^2 value of 0.97, indicating that the model was strongly consistent with the experimental data. This model is, therefore, reliable for determination of K_d within the experimental conditions covered in this study (i.e., TS concentrations of 0.5% to 2.5% and temperature range of 5°C to 35°C).

- In general, our empirical model on the effect of temperature on K_d showed good agreement with the Emerson et al. (1975) model for predicting K_d in pure water (R^2 of 0.99; fig. 8). However, the absolute values of K_d in the liquid dairy manure were less than those in pure water. This difference is attributed to the inhibition of NH_4^+ dissociation by the presence of TS in the liquid dairy manure. In addition, the effect of TS was more pronounced at elevated temperatures.

- Models of the K_d in dairy manures need to consider both, and simultaneously, the effects of manure temperature and total solids content to enhance model reliability.

- In order to initiate ammonia emissions mitigation strategies based on the effects of solids, ionic strength, or both on the K_d in dairy manure, it is important to conduct further studies to delineate the effects of suspended solids from those of ionic strength. In addition, it is important to determine if the suspended solids (or TS in general) characteristics resulting from different diets fed to animals have significant effects on the K_d in dairy manure.

REFERENCES

APHA. 1998. *Standard Methods for the Examination of Water and Wastewater.* 20th ed. Washington, D.C.: American Public Health Association.

Arogo, J., R. H. Zhang, G. L. Riskowski, L. L. Christianson, and D. L. Day. 1999. Mass transfer coefficient of ammonia in liquid swine manure and aqueous solutions. *J. Agric. Eng. Res.* 73(1): 77-86.

Arogo, J., P. W. Westerman, and Z. S. Liang. 2003. Comparing ammonium ion dissociation constant in swine anaerobic lagoon liquid and deionized water. *Trans. ASAE* 46(5): 1415-1419.

Bell, T. G., M. T. Johnson, T. D. Jickells, and P. S. Liss. 2007 Ammonia/ammonium dissociation coefficient in seawater: A significant numerical correction. *Environ. Chem.* 4(3): 183-186.

Clegg, S., and M. Whitfield. 1995. A chemical model of seawater including dissolved ammonia and the stoichiometric dissociation

constant of ammonia in estuarine water and seawater from -2° to 40°. *Geochim. Cosmochim. Acta* 59(12): 2403-2421.

De Visscher, A., L. A. Harper, P. W. Westerman, Z. S. Liang, J. Arogo, R. R. Sharpe, and O. Van Cleemput. 2002. Ammonia emissions from anaerobic swine lagoons: Model development. *J. Applied Meteorol.* 41(4): 426-433.

Emerson, K., R. C. Russo, R. E. Lund, and R. V. Thurston. 1975. Aqueous ammonia equilibrium calculations: Effect of pH and temperature. *J. Fish. Res. Board Canada* 32: 2379-2383.

Hashimoto, A. G., and D. C. Ludington. 1971. Ammonia desorption from concentrated chicken manure slurries. In *Livestock Waste Management: Proc. Intl. Symposium on Livestock Wastes*, 117-121. St. Joseph, Mich.: ASAE.

Jayaweera, G. R., and D. S. Mikkelsen. 1990. Ammonia volatilization from flooded soil systems: A computer model: I. Theoretical aspects. *SSSA J.* 54(5): 1447-1455.

Liang, Z. S., P. W. Westerman, and J. Arogo. 2002. Modeling ammonia emission from swine anaerobic lagoons. *Trans. ASAE* 45(3): 787-798.

Loehr, R. C. 1984. *Pollution Control for Agriculture.* 2nd ed. New York, N.Y.: Academic Press.

Montes, F., C. A. Rotz, and H. Chaoui. 2009. Process modeling for ammonia volatilization from ammonia solution and manure surfaces: A review with recommended models. *Trans. ASABE* 52(5): 1707-1719.

Ni, J. 1999. Mechanistic models of ammonia release from liquid manure: A review. *J. Agric. Eng. Res.* 72(1): 1-17.

SAS. 2006. *SAS User's Guide: Statistics.* Ver. 9.1.3. Cary, N.C.: SAS Institute, Inc.

Shaw, B. W. 1994. Use of a convective emission chamber to study particle re-suspension. PhD diss. Urbana, Ill.: University of Illinois, Department of Agricultural and Biological Engineering.

Silbey, R. J., A. A. Alberty, and M. G. Bawendi. 2005. *Physical Chemistry.* 4th ed. New York, N.Y.: Wiley.

Snoeyink, V. L., and D. Jenkins. 1980. *Water Chemistry.* New York, N.Y.: John Wiley and Sons.

Sommer, S. G., G. Q. Zhang, A. Bannink, D. Chadwick, T. Misselbrook, R. Harrison, N. J. Hutchings, H. Menzi, G. J. Monteny, J. Q. Ni, O. Oenema, and J. Webb. 2005. Algorithms determining ammonia emission from buildings housing cattle and pigs and from manure stores. *Advances in Agron.* 89: 261-335.

Sørensen, P., and M. Amato. 2002. Remineralisation and residual effects of N after application of pig slurry to soil. *European J. Agron.* 16(2): 81-95.

Zhang, R. H. 1992. Degradation of swine manure and a computer model for predicting the desorption rate of ammonia from an under-floor pit. PhD diss. Urbana, Ill.: University of Illinois, Department of Agricultural and Biological Engineering.