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Mass transfer coefficients of ammonia for liquid dairy manure

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HIGHLIGHTS

► The mass transfer coefficient (K_{OL}) of ammonia (NH_3) increased with liquid temperature (T_L) and air velocity (V_{air}).
► The K_{OL} decreased with increases in air temperature (T_{air}) and total solids (TS) concentration.
► The K_{OL} sensitivity to key factors, in descending order, was: T_L, T_{air}, V_{air}, and TS concentration.

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ABSTRACT

Available data indicate that 75–80% of total nitrogen entering a dairy operation is lost as ammonia (NH_3) via manure storage systems such as anaerobic lagoons. Direct measurement of NH_3 emissions from manure holding systems can be complicated and expensive; however, process-based emission models can provide a cost-effective alternative for estimating NH_3 emissions. The overall NH_3 mass transfer coefficient (K_{OL}) is an important component of any NH_3 emission process-based model. Models relying purely on theoretically-derived mass transfer coefficients have not adequately predicted NH_3 emissions from livestock manure, and these values are lacking in general for liquid dairy manure handling systems. To provide critically needed K_{OL} data for dairy facilities, this study directly measured NH_3 loss from dilute dairy manure slurries placed in a laboratory convective emission chamber to determine realistic NH_3 K_{OL} values under conditions typically experienced in the Pacific Northwest. The K_{OL} values increased as liquid temperature and air velocity increased and decreased as air temperature and total solids content increased, exhibiting an overall range of 1.41×10^{-6}–3.73×10^{-6} m s^{-1}. These values were then used to develop a non-linear empirical model of K_{OL} for dilute dairy manure slurries ($R^2 = 0.83$). The K_{OL} exhibited sensitivity to the four model parameters considered in descending order: liquid manure temperature, ambient air temperature, wind or air velocity, and total solids concentration. The suite of K_{OL} values applicable to liquid dairy manure and the establishment of an empirical model that yields accurate K_{OL} estimates under a range of conditions for use in process-based models provide valuable tools for predicting NH_3 emissions from dairy operations.

1. Introduction

Agriculture is the largest source of global ammonia (NH_3) emissions, with livestock production accounting for ~80% of this total flux (De Visscher et al., 2002; Aneja et al., 2000; Sommer and Hutchings, 1995; Battye et al., 1994). Seventy to 85% of the total nitrogen (total-N) entering an anaerobic lagoon can be lost via gaseous emissions, as opposed to 10–55% for other types of livestock manure storage systems (MWPS, 2001). Similarly, the US EPA estimates that dairy lagoons lose 71% of total-N when calculating NH_3 volatilization as part of the National Emission Inventory (EPA, 2004). Thus, it is clear that anaerobic lagoons significantly contribute to NH_3 emissions originating from dairy operations. This is a concern because emitted NH_3 not only pollutes the environment (Ullman and Mukhtar, 2007; Paerl and Whitall, 1999), but the corresponding N loss also lowers the fertilizer-value of the residual manure (Vaddella et al., 2011; Ndegwa et al., 2008).

Determining NH_3 emissions from agricultural facilities is critical to appropriately regulate emissions from livestock operations to protect the environment. Direct measurement of NH_3 fluxes from manure storage facilities, however, can be challenging, time consuming, and expensive (Liang et al., 2002). Since NH_3

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volatilization is governed by both manure characteristics and environmental or meteorological conditions, this onerous task has to be performed for each separate livestock operation because no two facilities will be similar in all respects. Process-based emission models offer an alternative, cost-effective approach for estimating NH_3 emissions from such systems, because process-based models generally only require values for key manure, environmental and meteorological parameters to effectively predict NH_3 volatilization rates for the system in question.

A generic process-based model for NH_3 emissions from bulk liquid manure can be expressed as:

$$Q_a = K_{OL}A([NH_3]_L - [NH_3]_a) \tag{1}$$

Where Q_a = ammonia flux (g s^{-1}), K_{OL} = overall convective mass transfer coefficient for ammonia (m s^{-1}), A = area of emitting surface (m^2), $[NH_3]_L$ = ammonia concentration at the lagoon liquid surface (g m^{-3}), and $[NH_3]_a$ = ammonia concentration in air (g m^{-3}) (Ni, 1999). Two key input parameters required in Equation (1) are the K_{OL} for NH_3 and $[NH_3]_L$. In general, $[NH_3]_a$ is very small and is neglected. Total ammonia nitrogen (TAN) is the sum of NH_3 and ammonium (NH_4^+) concentrations. In aqueous solutions, equilibrium exists between unionized NH_3 and ionized NH_4^+. This equilibrium is governed by NH_4^+ dissociation constant (K_d) which is a function of liquid temperature. The K_{OL} describes the NH_3 transfer rate from the liquid surface to the free air stream, while the K_d value represents the volatile NH_3 fraction of the TAN present in the bulk liquid. The K_{OL} value for the liquid manure depends on several factors, including the liquid TAN concentration, pH, liquid and ambient air temperatures, solids concentration, and wind speed (De Visscher et al., 2002; Arogo et al., 1999; Ni, 1999). Arogo et al. (1999) modeled K_{OL} for an anaerobic under-floor swine manure pit using data from a series of laboratory experiments conducted in a convective emissions chamber and showed that air flow velocity (V_{air}), lagoon-liquid temperature (T_L), and air temperature (T_{air}) influenced K_{OL}. However, their model did not consider the contribution of the solids on the K_{OL}, which other researchers have indicated is a significant factor impacting NH_3 volatilization rates (De Visscher et al., 2002; Zhang et al., 1994).

Although studies focused on establishing empirical K_{OL} models for livestock manure exist, primary emphasis has been placed on swine lagoons and little attention has been given to dairy manure storage systems (Ni, 1999). As an alternative, research has relied more on theoretical approaches to determining mass transfer coefficients for anaerobic dairy lagoons. For instance, Rumburg et al. (2008) compared direct measurements of NH_3 emissions with predictions generated by a process-based model that used theoretical and empirical K_{OL} values reported from Ni (1999) for dairy manure. The results of this study revealed that theoretically derived K_{OL} values exhibited a significantly wider range of errors (120% normalized mean error (NME)) compared with empirical values (21% NME). Because theoretical K_{OL} derivations for livestock wastewaters are inadequate and empirical K_{OL} values are largely lacking for dairy wastewaters (Montes et al., 2009; Ni, 1999), an empirical K_{OL} model for dairy wastewater is critically needed to enhance NH_3 emission models. The overall objective of this research was to develop a statistical model using experimentally derived NH_3 mass transfer coefficients for dairy wastewater to improve the reliability of NH_3 emission process-based models applications in liquid dairy manure systems.

2. Materials and methods

2.1. Theory behind K_{OL} determination

Ammonia release from anaerobic dairy lagoon wastewater depends on the resistance of its transfer and the concentration gradient between the lagoon liquid and the atmosphere (Arogo et al., 1999) as indicated by Equation (1). Fig. 1 offers a conceptual process of NH_3 release from an anaerobic dairy lagoon.

Fig. 1 shows NH_3 emissions from the bulk liquid manure into the atmosphere is influenced by the Henry's constant (k_H) and convective mass transfer (k_C) in gaseous phase. The K_{OL} for NH_3 is a function of k_H and k_C. The effect of diffusion mass transfer (k_D) is negligible compared to K_{OL} and this term is usually disregarded in most process models. In addition, the NH_3 concentration in the air is also insignificant compared with its concentration in the liquid, especially for open-surface storages. Equation (1) can thus be rewritten as Equation (2), where t is the time step and the negative sign indicates that NH_3 concentration in the liquid matrix decreases with time. Equation (2) can further be simplified to Equation (3) by noting that $M_{TAN} = V \times TAN$, where V = volume of manure (m^3) and TAN = the total ammoniacal nitrogen concentration (g m^{-3}).

$$\frac{dM_{TAN}}{dt} = -K_{OL}A[NH_3]_L \tag{2}$$

$$\frac{dTAN}{dt} = -K_{OL}\frac{A}{V}[NH_3]_L \tag{3}$$

Equation (3), however, cannot be solved because it is impossible to measure the concentration of free NH_3 in the wastewater. Substituting $\alpha \times$ TAN for $[NH_3]_L$ in Equation (3) and integrating translates into Equation (4), where α is the unionized (NH_3) fraction of TAN in the liquid manure, and $TAN_{0,L}$ and TAN_t are the initial and current TAN concentrations in the bulk liquid manure at a given time t, respectively. At liquid pH values above 11.0, all of the TAN is in the form of free NH_3 and hence $\alpha = 1$ (see Fig. 2). The logarithmic

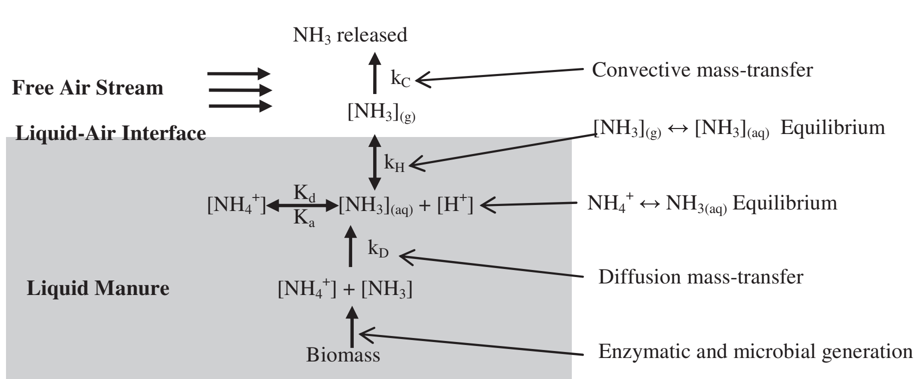

Fig. 1. Ammonia release mechanism from liquid manure (Ni, 1999).

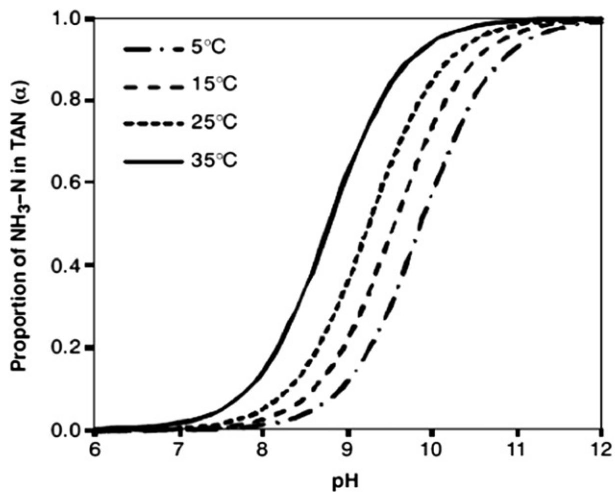

Fig. 2. Function of NH_3/NH_4^+-equilibrium with temperature and pH in aqueous solutions (Vaddella et al., 2011).

form of Equation (4), as shown in Equation (5), is a more preferable form because for $\alpha = 1$ and a known A and V, K_{OL} is computable from the slope of linear regression plot.

$$\mathrm{TAN}_t = \mathrm{TAN}_{0,L} \times e^{-\left(K_{OL}\alpha\frac{A}{V}\right)t} \quad (4)$$

$$\ln\left(\frac{\mathrm{TAN}_t}{\mathrm{TAN}_{0,L}}\right) = -K_{OL}\alpha\frac{A}{V}t \quad (5)$$

2.2. Apparatus

A convective emission chamber was used to evaluate the impacts of relevant environmental parameters on NH_3 volatilization rates to establish an empirical K_{OL} model. Fig. 3 is a photograph of the chamber, which is similar to units used in previous studies (Arogo et al., 1999; Shaw, 1994; Zhang, 1992). The convective emission chamber consisted of a blower, a flow-controller unit, two screens (3 mm stainless steel, 120 cm apart) to create turbulence, and a sample-chamber. The overall chamber dimensions were 4.2 m × 0.45 m × 0.15 m ($L \times W \times H$) and the test section dimensions were 1.2 m × 0.45 m × 0.15 m ($L \times W \times H$). The chamber walls were insulated and two thermocouples were used to control the T_{air} within ±1 °C. The V_{air} was controlled within ±0.1 m s^{-1} using a damper at the inlet of the air generator. The sample test-pan (27.9 cm L × 17.8 cm W × 3.5 cm H) was placed in a constant temperature water bath to maintain set temperatures during the experiments. The water bath also maintained specified temperatures within ±1 °C.

2.3. Experimental design

The K_{OL} values were determined under the following randomized conditions:

1. Air temperatures: 15, 25, and 35 °C;
2. Air velocities: 0.5, 1.0, 1.5, 2.5, and 4.0 m s^{-1};
3. Manure liquid temperatures: 5, 15, 25 and 35 °C; and
4. Total solid concentrations: 0.5, 1.0, 1.5, 2.0, 2.5% (w/w basis); typical TS values for dairy lagoon liquid (Mukhtar et al., 2004).

Dairy manure (with concentration of TS of ~3.0% and 500 mg L^{-1} TAN) was obtained from Washington State University Knott Dairy Research Center, Pullman, WA. The manure samples were diluted to the desired TS concentrations using tap water, and the pH was subsequently adjusted to 12.0 using 10 M NaOH to ensure that all TAN was in the form of free NH_3 (i.e., $\alpha = 1$ as shown in Fig. 2). The prepared manure sample was poured into the test pan, which was placed in the water-bath and allowed to attain the specified liquid-temperature. The temperature of the manure sample was checked frequently with a thermometer to ensure constant temperature conditions were maintained. The convective

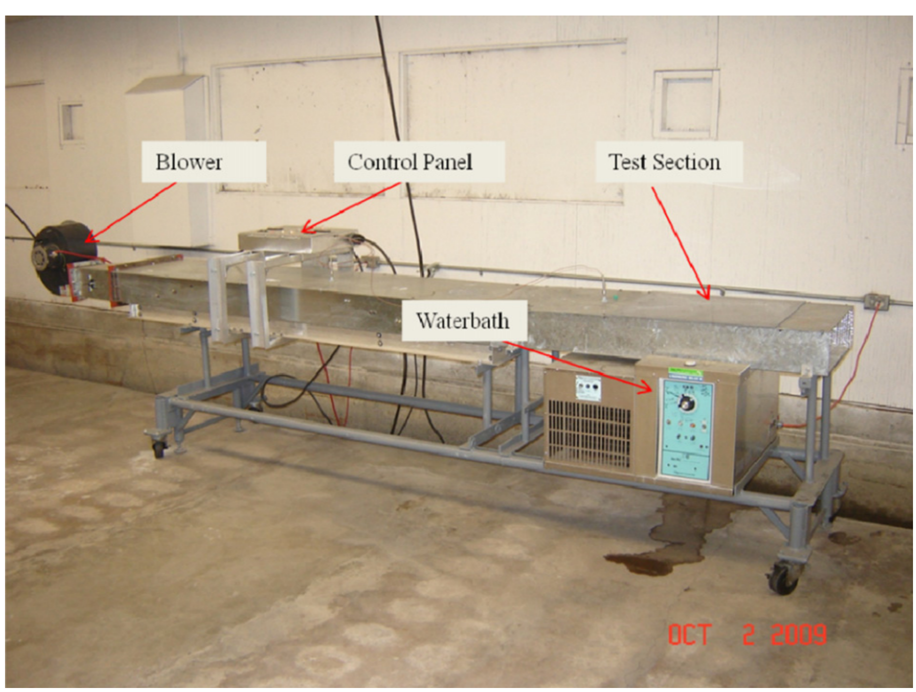

Fig. 3. The convective emission chamber: a photograph of the chamber.

emission chamber was run for another 30 min to allow the manure sample to stabilize to the test conditions. Once the manure attained the desired test conditions, 1 mL samples were drawn 2 mm below the liquid surface at 5 locations in the test pan every 30 min for 4 h. To prevent further NH_3 loss, 5 mL of 2 M sulfuric acid was added to each collected sample. The samples were analyzed immediately after the experiment using the Hach Nessler colorimetric method 8033 adapted from standard methods 4500-NH_3 (APHA, 1992, 2005). Each test-condition was replicated 3 times.

The test-conditions examined in this study are shown in Table 1. These conditions represent expected dilute manure characteristics found in anaerobic dairy lagoons (and other similar storages) and environmental conditions typically encountered in the US Pacific Northwest.

3. Model development and data analysis

3.1. Model development

Several modeling approaches for determining K_{OL} values for livestock wastewaters and pure water are documented in literature (Liu et al., 2008; Guo and Roache, 2003; Arogo et al., 1999; Haslam et al., 1924). Guo and Roache (2003) modeled K_{OL} using six different organic compounds in laboratory convective emission chambers using the Sherwood number (dimensionless) approach as illustrated in Equations (6)–(9), where S_h = Sherwood number, also represented as Equation (7), R_e, and S_c are Reynolds (Equation (8) and Schmidt (9)) numbers respectively, $C_{K_{OL}}$ is a constant of K_{OL}, a and b are exponents, K_{OL} is the overall mass transfer coefficient, L is characteristic length, $D_{A\text{-air}}$ is NH_3 diffusivity in air, ρ_{air} is the density of air, V_{air} is the air velocity, and μ_{air} is the coefficient of dynamic viscosity of air.

$$S_h = C_{K_{OL}}(R_e)^a(S_c)^b \tag{6}$$

$$S_h = \frac{K_{OL}L}{D_{A\text{-air}}} \tag{7}$$

$$R_e = \frac{\rho_{air}V_{air}L}{\mu_{air}} \tag{8}$$

$$S_c = \frac{\mu_{air}}{\rho_{air}D_{A\text{-air}}} \tag{9}$$

Haslam et al. (1924) developed a mass transfer coefficient model for NH_3 in pure water taking two factors, V_{air} and T_L, into consideration. Arogo et al. (1999) determined that K_{OL} in swine manure was directly proportional to V_{air} and T_L, and inversely proportional to T_{air}. In this study, empirical K_{OL} values obtained from a series of studies conducted using a convective emission chamber were considered as the basis for formulating an equation for the K_{OL} for dairy manure slurries. First, Equation (10) was conceived considering all the factors included in obtaining the empirical K_{OL} values. Second, Equations (11) and (12) were formulated by noting that: (i) K_{OL}s increase with an increase in V_{air} and T_L, and (ii) K_{OL} values decrease with an increase in T_{air} and TS concentration. $C_{K_{OL}}$ is a constant of proportionality and a, b, c, and d are respective exponents.

$$K_{OL} = f\{T_L, T_{air}, V_{air}, \mathrm{TS}\} \tag{10}$$

$$K_{OL} \propto \frac{(T_L)^a(V_{air})^b}{(\mathrm{TS})^c(T_{air})^d} \tag{11}$$

$$K_{OL} = C_{K_{OL}}\frac{(T_L)^a(V_{air})^b}{(\mathrm{TS})^c(T_{air})^d} \tag{12}$$

3.2. Data analysis

Ammonia fluxes from the manure samples placed in the convective emission chamber for the respective environmental conditions were used to generate the empirical K_{OL} data. The constants $C_{K_{OL}}$, a, b, c, and d in Equation (12) were obtained using Proc NLIN SAS (SAS Institute Inc, 2006). Proc NLIN is the SAS procedure for fitting nonlinear regression models. The relevance of using Proc NLIN method is presented in the Results and discussion section.

4. Results and discussion

4.1. The K_{OL} computations

The K_{OL} values were calculated from the estimated slope of the non-linear regression plots of the exponential TAN concentration decay in the liquid dairy manure over the test period (240 min) according to Equation (5). The K_{OL} values obtained from regression analyses for NH_3 with their respective R^2 values at different environmental conditions are presented in Table 2. For instance, Fig. 4

Table 1
Experimental conditions used to determine overall mass transfer coefficients for ammonia in liquid dairy manure.

Run #	Air temperature (°C)	Air velocity (m s^{-1})	Liquid temperature (°C)	Solids content (%, w/w)
1	25	0.5	25	1.5
2	25	1	25	1.5
3	25	1.5	25	1.5
4	25	2.5	25	1.5
5	25	4	25	1.5
6	25	1.5	5	1.5
7	25	1.5	15	1.5
8	25	1.5	35	1.5
9	25	1.5	25	0.5
10	25	1.5	25	1.0
11	25	1.5	25	2.0
12	25	1.5	25	2.5
13	15	1.5	25	1.5
14	35	1.5	25	1.5

Table 2
Respective K_{OL} values for NH_3 at different manure and environmental conditions examined in this study.

Parameter	Parameter value	$K_{OL} \times 10^{-6}$, m s^{-1}	R^2-value
Air temperature, °C	15	2.65	0.97
	25	2.16	0.96
	35	1.81	0.99
Liquid temperature, °C	5	1.41	0.99
	15	1.77	0.99
	25	2.16	0.96
	35	3.73	0.95
Air velocity, m s^{-1}	0.5	1.30	0.98
	1.0	1.59	0.98
	1.5	2.17	0.96
	2.5	2.10	0.99
	4.0	3.13	0.97
TS concentration, %	0.5	3.03	0.98
	1.0	2.41	0.99
	1.5	2.16	0.97
	2.0	2.21	0.96
	2.5	2.02	0.98
	3.0	3.03	0.98

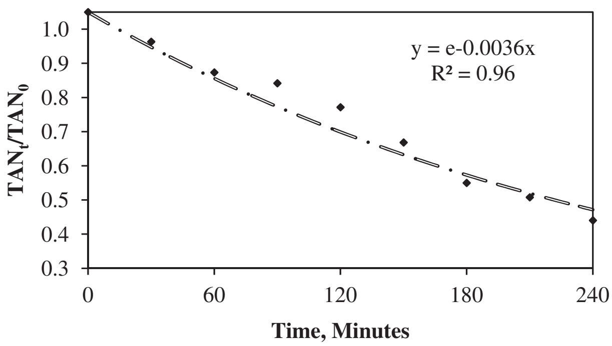

Fig. 4. TAN decay residuals curve for dairy manure at T_L = 25 °C, T_{air} = 25 °C, V_{air} = 1.5 m s^{-1}, TS = 1.5%, and pH 12.

provides a representative test run conducted at T_L = 25 °C, T_{air} = 25 °C, V_{air} = 1.5 m s^{-1}, TS = 1.5%, and a pH of 12. The TAN concentration residual curve followed first-order reaction kinetics ($R^2 = 0.96$). The resultant K_{OL} was calculated to be 2.1 × 10^{-06} m s^{-1}. This procedure of computing the K_{OL} values was repeated for all the other test-conditions examined in this study to generate K_{OL} data (Table 2) for modeling NH_3 K_{OL} for dairy manure within the test-conditions.

In general, the TAN decay curves for liquid dairy manure were similar under constant TS concentrations, T_{air}, and V_{air} at liquid manure temperatures (T_L) of 5, 15, 25, and 35 °C and followed the trend shown in Fig. 5. All the decay curves of the TAN concentration similarly followed first-order reaction rates with coefficients of determination (R^2) ranging from 0.95 to 0.99. A general tendency wherein K_{OL} increased with increasing liquid manure temperature was observed. A similar trend was reported by Arogo et al. (1999) for K_{OL} in swine manure. Ni (1999) reported K_{OL} values ranged from 1.3 × 10^{-06} to 11.7 × 10^{-03} m s^{-1} for swine manure in a review of multiple studies. The results obtained from this study (1.41 × 10^{-06} to 3.73 × 10^{-06} m s^{-1}) fell within this broad span, but displayed a considerably narrower range.

4.2. Effect of liquid temperature (T_L) on K_{OL}

Fig. 6 presents the K_{OL} values for NH_3 in liquid dairy manure at the four liquid temperatures (at fixed: air velocity of 1.5 m s^{-1}, TS concentrations of 1.5%, and at air temperature of 25 °C) examined in this study and the corresponding regression analysis showing the effect of T_L on K_{OL}. In general, the K_{OL} increased exponentially with an increase in the liquid temperature. Similar trends were observed

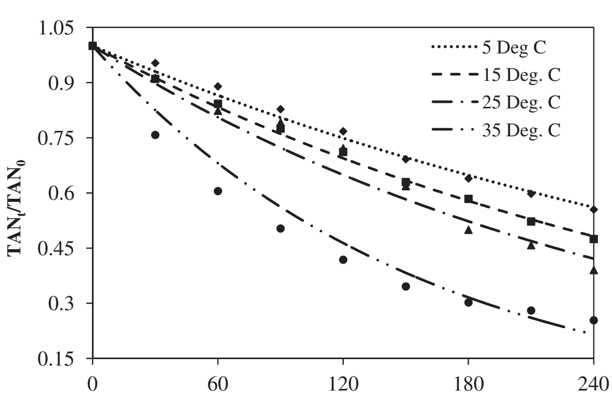

Fig. 5. Ammonia decay curves over a period of 4 h at 12 pH, air velocity 1.5 m s^{-1}, TS concentrations 1.5%, and at liquid temperature 25 °C.

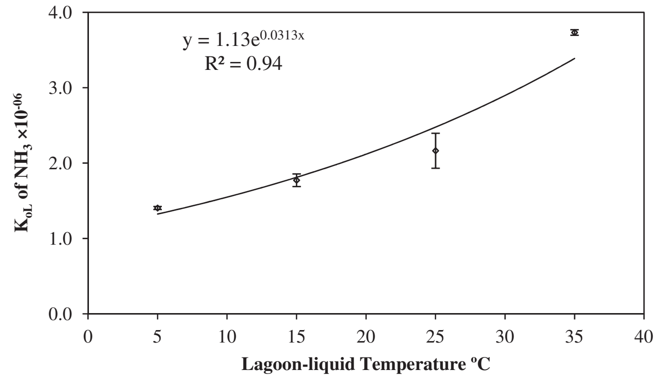

Fig. 6. K_{OL} as a function of liquid temperature at T_{air} = 25 °C, V_{air} = 1.5 m s^{-1}, TS = 1.5% (error bars indicate standard deviations from means based on triplicate tests).

for K_{OL} values determined for swine manure in earlier studies (Arogo et al., 1999). In summary, as liquid temperature increases the free NH_3 fraction increases exponentially, and consequently the potential of NH_3 emission into the environment is enhanced. Consequently, ammonia emissions from the anaerobic dairy lagoons and other similar facilities are, generally, higher in warm seasons and during the day, and lower in colder seasons and at night (Todd et al., 2011; Blunden and Aneja, 2008; Aneja et al., 2001, 2000).

4.3. Effect of air velocity (V_{air}) on K_{OL}

The overall mass transfer coefficient for NH_3 as a function of air velocity (V_{air}) at T_{air} of 25 °C, T_L of 25 °C, and a TS concentration of 1.5% is shown in Fig. 7. Based on the linear regression plot ($R^2 = 0.92$), we infer that the K_{OL} for liquid dairy manure is directly proportional to the air velocity above the liquid–air interface. This relationship is consistent with theoretical expectations, because higher wind velocities result in more rapid transfer of NH_3 away from the air space above the liquid–air interface. Transport of NH_3 away from the air above the liquid–air interface reduces NH_3 partial pressure and leads to enhanced volatilization. In essence, a greater NH_3 concentration gradient results; a governing factor for NH_3 loss in Equation (1). This implies that manure storage facilities located in areas exposed to stronger winds will experience elevated NH_3 emissions (Misselbrook et al., 2005; Arogo et al., 1999).

4.4. Effect of air temperature (T_{air}) on K_{OL}

The relationship between K_{OL} and air temperature at T_L = 25 °C, V_{air} = 1.5 m s^{-1}, and TS = 1.5%, is shown in Fig. 8. The high

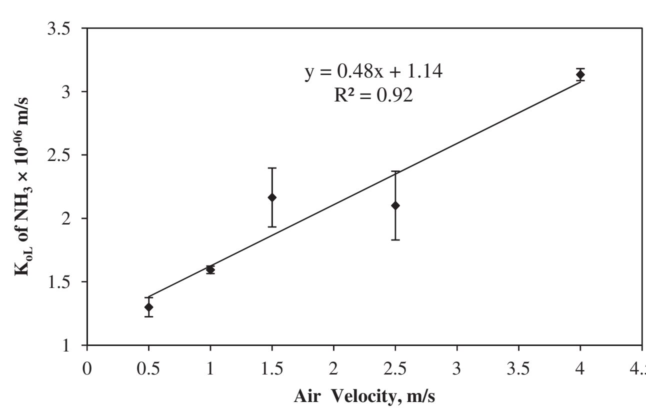

Fig. 7. Relationship between K_{OL} and air velocity at T_L = 25 °C, T_{air} = 25 °C, TS = 1.5% (error bars indicate standard deviations from means based on triplicate tests).

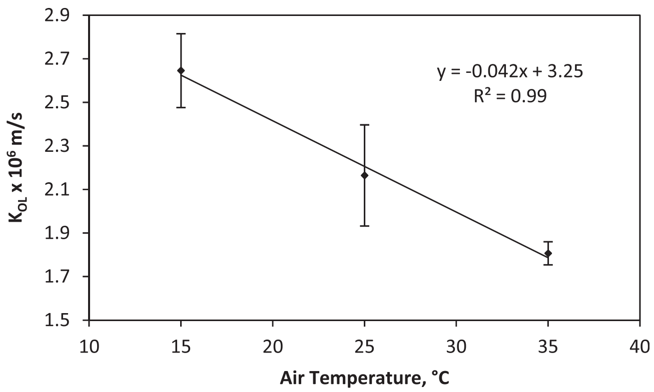

Fig. 8. K_{OL} as a function of air temperature at $T_L = 25$ °C, $V_{air} = 1.5$ m s^{-1}, and TS = 1.5% (error bars indicate standard deviations from means based on triplicate tests).

correlation of determination (R^2) of 0.99 indicates that K_{OL} decreases with an increase in air temperature. This finding reflects the increase of dynamic viscosity (μ) of air with an increase in ambient temperature. This phenomenon in turn increases resistance to NH_3 volatilization from the emitting surface. However, while higher air temperatures offer more resistance to NH_3 air pollution when considered alone, a corresponding increase in liquid temperature will result which promotes NH_3 emissions. Results of this study indicate a 1.4-fold increase in K_{OL} for every 10 °C rise in T_L and a 1.2-fold decrease for every 10 °C rise in T_{air}. This finding suggests that NH_3 volatilization rates from dairy manure are impacted more by the liquid temperature if both T_L and T_{air} increase by the same magnitude.

4.5. Effect of total solids concentration (TS) on K_{OL}

The effect of TS concentration at $T_L = 25$ °C, $T_{air} = 25$ °C, and $V_{air} = 1.5$ m s^{-1}, on K_{OL} for dairy manure is presented in Fig. 9. The fitted exponential decay plot seems to adequately fit the experimental data ($R^2 = 0.81$). Consequently, while the K_{OL} values for the liquid dairy manure decreased with increase in the TS concentration, in general, the effects at lower TS concentrations are greater than at higher TS concentrations. In previous research, Arogo et al. (1999) observed no significant effect of the TS concentration on the K_{OL} from liquid swine manure when the TS concentration was lower than 1.0%. This study, however, indicates suspended solids in liquid dairy manure can impede NH_3 volatilization, which conforms to the assertions made by De Visscher et al. (2002). The latter researchers indicated that NH_4^+ adsorption on suspended organic solids reduced the diffusion coefficient resulting in lower NH_3 loss.

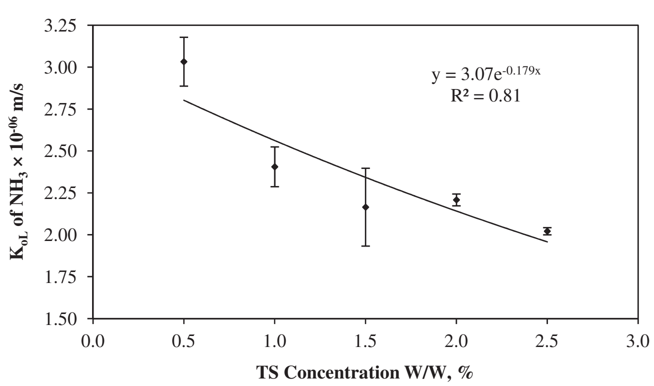

Fig. 9. Effect of total solids on K_{OL} at $T_L = 25$ °C, $T_{air} = 25$ °C, and $V_{air} = 1.5$ m s^{-1} (error bars indicate standard deviations from means based on triplicate tests).

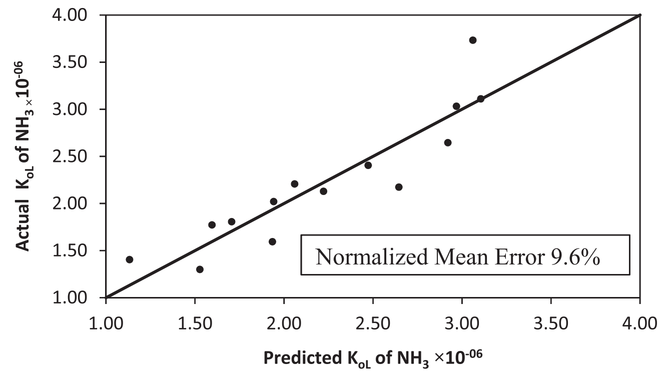

Fig. 10. Comparison of the actual and the predicted K_{OL} values in dairy manure slurries.

4.6. Our overall mass transfer model

The K_{OL} data (see Table 2) for dairy manure obtained from this laboratory study, with respect to variables T_L, V_{air}, TS, and T_{air}, were used in Proc NLIN SAS program to solve for the values of constants a, b, c, d and $C_{K_{OL}}$ in Equation (12). The respective constants obtained from Proc NLIN are displayed in Equation (13) represents the best non-linear regression fit to the K_{OL} experimental data. The strong coefficient of determination of this model ($R^2 = 0.83$) indicates consistency with the experimental data, providing a reliable tool for determining NH_3 K_{OL} values for liquid dairy manure slurries, provided manure characteristics and environmental conditions are within the ranges evaluated in this study.

$$K_{OL} = 4.85 \times 10^{-11} \frac{(T_L)^{9.7}(V_{air})^{0.34}}{(T_{air})^{8.02}(TS)^{0.26}} \quad (13)$$

Fig. 10 displays a plot comparing measured and model predicted K_{OL} values of NH_3 for liquid dairy manure. The results indicate good agreement between the measured and the predicted K_{OL} values with a normalized mean error (NME) of 9.6% which was calculated using Equation (14):

$$NME = \frac{\sum_1^n |X_{mod} - X_{mea}|}{\sum_1^n X_{mea}} \times 100\% \quad (14)$$

where n is the number of data values, while X_{mod} and X_{mea} are the modeled and measured K_{OL}, respectively.

4.7. Sensitivity analysis

Sensitivity analysis was performed by increasing respective variables by 10% within the range of experiment conditions. Sensitivity analysis showed K_{OL} exhibited sensitivity to the factors considered in descending order: T_L, T_{air}, V_{air} and TS concentration (Table 3). To test the combined sensitivity of these parameters on

Table 3
Sensitivity analysis of the predicted fluxes by the model.

Model parameter	10% Change within parameter range[a]	K_{OL} sensitivity (%)
T_L °C	2.5	7.9
V_{air} m s^{-1}	0.15	3.2
T_{air} °C	2.5	−5.9
TS %	0.15	−2.5

T_L = Lagoon-liquid temperature; T_{air} = Air temperature; V_{air} = Air velocity; TS = Total solids concentration w/w.

[a] Standard parameter range: $T_L = 25$ °C, $T_{air} =$ °C, $V_{air} = 25$ °C, TS content = 1.5%.

K_{OL} of NH_3 all variable were increased simultaneously by 10%, which resulted in K_{OL} increasing by 2.2%. This analysis indicates that T_L and V_{air} exert a greater impact on NH_3 emissions from dairy lagoons than T_{air} and TS when all parameters increase simultaneously by the same percentage.

5. Summary and conclusions

The overall mass transfer coefficient of NH_3 for bulk liquid dairy manure to the air was empirically modeled using data from a series of experiments performed in a laboratory convective emission chamber. The following conclusions were drawn from the experimental results and the associated modeling process:

1. K_{OL} values increased with an increase in liquid temperature and an increase in air velocity, but decreased with an increase in air temperature under the conditions tested. These findings correspond with expected results and agree with similar studies that have examined NH_3 emissions from other types of livestock liquid manure management systems.
2. The K_{OL} decreased with an increase in TS concentration in the range of 0.5–2.5%, which suggests that solids impede the mass transfer of NH_3 from liquid dairy manure. Other researchers have reported conflicting findings in regards to the impact of TS on K_{OL} values. However, the relationship between K_{OL} and TS appeared to resemble a second-order reaction, but they better fitted with first-order kinetics and the difference between K_{OL} values was most pronounced between 0.5 and 1.0% TS.
3. The developed model for predicting the K_{OL} of NH_3 from liquid dairy manure exhibited an NME of 9.6%, which demonstrates a good fit with the experimental data.
4. K_{OL} exhibited sensitivity to the four model parameters considered in descending order: liquid manure temperature, ambient air temperature, wind or air velocity, and total solids concentration.

The suite of NH_3 mass transfer coefficients determined in this study provides measured values applicable to liquid dairy manure handling systems, and fills a gap in knowledge for this livestock sector. Moreover, the establishment of an empirical model that yields accurate K_{OL} estimates under a range of conditions provides a functional tool for use in process-based models used to predict NH_3 emissions. These findings will help improve our understanding of NH_3 volatilization from dairy operations and help develop approaches to mitigate emissions to the environment.

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