Mass Transfer Coefficient of Ammonia in Liquid Swine Manure and Aqueous Solutions

J. Arogo¹; R. H. Zhang²; G. L. Riskowski³; L. L. Christianson³; D. L. Day³

¹Biosystems and Agricultural Engineering, Oklahoma State University, Stillwater, OK 74078, USA; e-mail: arogok@okstate.edu
²Biological and Agricultural Engineering, University of California, Davis, CA 95616, USA
³Agricultural Engineering Department, University of Illinois, Urbana, IL 61801, USA

(Received 24 November 1997; accepted in revised form 6 November 1998)

Correlations for the overall mass transfer coefficient of ammonia with liquid properties and environmental conditions were developed for ammonia volatilizing from aqueous solutions as well as from liquid manure in a convective emission chamber where the air velocity, temperature, turbulence, and relative humidity were precisely controlled.

The mass transfer coefficient was observed to increase with increasing air velocity and liquid temperature but decreased with increasing air temperature. Analysis of air-liquid temperature combinations on the influence of mass transfer coefficient using the correlation equations showed that a lower air temperature (15°C) and higher liquid temperature (35°C) combination is more likely to result in higher ammonia volatilization rates compared to other temperature combinations. On the other hand, a higher air temperature (35°C) and lower liquid temperature (15°C) combination would result in lower ammonia volatilization rates for different air velocities.

The mass transfer coefficient for ammonia was much more sensitive to changes in air velocity at lower compared to higher velocity ranges. Similar sensitivity responses were obtained for both air and liquid temperature ranges.

1. Introduction

Air quality in livestock buildings is a major concern for livestock producers because it influences the well-being of both animals and workers. The concern is especially serious in environmentally controlled swine buildings where liquid manure is stored in under-floor pits. The stored manure undergoes microbial degradation resulting in production of gases such as: methane, CH₄; hydrogen sulphide, H₂S; carbon dioxide, CO₂; ammonia, NH₃; and volatile organic compounds, VOCs. These gases, as well as dust, are the major causes of indoor air contamination.

Ventilation is the primary method used to control the air quality in livestock buildings. It removes moisture and heat from respiring animals and other air contaminants generated within the building. The current design procedures for ventilation systems are based on moisture and heat balance requirements and do not sufficiently consider the release of manure pit gases. In order to increase the ventilation effectiveness and create a more desirable indoor environment, especially with respect to manure pit gases, more information about the production and release rates of manure pit gases is needed.

The release rate of gases from liquid manure is influenced by both manure properties (temperature and solids content) and environmental conditions (air temperature and velocity). Increasing air velocity and manure temperature has been shown to increase gas transfer rates across the liquid manure-air interface. In confined swine buildings, the air velocity above the manure surface will change as the ventilation requirement for the building changes. Also, the indoor air temperature will change as the outdoor air temperature changes depending on the ventilation system used. How these factors interact to influence the release of ammonia from stored liquid swine manure into the air is the subject of this study. Note, however, that the results for ammonia release will not provide predictions for the other manure pit gases. Separate studies are needed to determine the release rates for the other manure pit gases.

The objectives of this study were to (1) determine the overall mass transfer coefficient of ammonia transferring from liquid swine manure into the air under different environmental conditions and (2) develop a correlation between the mass transfer coefficient of ammonia and the pertinent manure properties and environmental conditions.
driving force: of a mass transfer rate constant and a concentration unit time is considered to be proportional to the product a volatile compound in the bulk liquid concentration per of these models, the rate of change of the concentration of ammonia volatilization at the liquid containment. For example, for swine con to determine ammonia concentration in the indoor air. Also, factors that a ect the solubility of a gas in a liquid will affect the mass transfer rate of the gas. Gases become less soluble with increasing liquid temperature and the presence of other solutes may also have negative effects on gas solubility. The results of this study will be used in models to predict ammonia release rate from any liquid manure storage, if the concentration of ammonia in the manure is known, the results could be used to estimate the ammonia release from the lagoon surface into the atmosphere.

2. Theoretical considerations

2.1. Mass transfer mechanisms and models for ammonia volatilization at the liquid–gas interface

Volatile compounds such as ammonia, carbon dioxide, and hydrogen sulphide partition themselves between the liquid and the gas above the liquid. Several models are available which describe interface mass transport. In all of these models, the rate of change of the concentration of a volatile compound in the bulk liquid concentration per unit time is considered to be proportional to the product of a mass transfer rate constant and a concentration driving force:

\[
\frac{dM}{dt} = KA_0(C_L - C_{air}) \tag{1}
\]

where \(M\) is the mass of the volatile compound in kg, \(K\) is the overall mass transfer coefficient of the volatile compound in m/s, \(A_0\) is the interfacial surface area in m\(^2\), \(C_L\) is the concentration of volatile compound dissolved in the liquid in g/l, \(C_{air}\) is the concentration of the volatile compound in the air in g/l, and \(t\) is time in seconds.

Assuming that the atmosphere acts as a sink for the volatile compound, the equilibrium concentration in the air can be calculated using Henry’s law, i.e., \(C_{air} = H C_L\), where \(H\) is the Henry’s law constant for the volatile compound.

In general, the mass transfer rate of a substance through an interfacial boundary layer is affected by the system geometry, physicochemical, and hydrodynamic properties of the two phases and the transferring substance. Also, factors that affect the solubility of a gas in a liquid will affect the mass transfer rate of the gas. Gases become less soluble with increasing liquid temperature and the presence of other solutes may also have negative effects on gas solubility.

In a detailed review of the theoretical gas transfer models that have been used to study ammonia volatilization, Zhang reported that Eqn (1) is most commonly used. Equation (1) is based on the two-film theory and is the simplest method to describe the mechanism of gas volatilization from a liquid to the open atmosphere. In

### Notation

- \(A_0\): interfacial surface area, m\(^2\)
- \(C_{air}\): concentration of the dissolved volatile compound found in the air, g/l
- \(C_L\): concentration of the dissolved volatile compound in the liquid, g/l
- \(C_K\): constant
- \(D\): diffusivity of a volatile compound in air, m\(^2\)/s
- \(D_{air}\): diffusivity of ammonia in air, m\(^2\)/s
- \(H\): Henry’s constant for the dissolved volatile compound
- \(K\): overall mass transfer coefficient for the dissolved volatile compound, m/s
- \(K_{OL}\): overall mass transfer coefficient for ammonia, m/s
- \(L\): characteristic length of the convective emission chamber, m
- \(M\): mass of the dissolved volatile compound, kg
- \(M_A\): molecular weight of ammonia, g/mol
- \(M_{air}\): molecular weight of air, g/mol
- \(M_{TAN}\): mass of total ammonia in given volume of liquid, kg
- \([NH_3]_L\): free ammonia concentration in solution, g/l
- \([NH_3]_{air}\): free ammonia concentration in the air, g/l
- \([NH_4^+]\): ammonium ion concentration, g/l
- \(P\): atmospheric pressure, atm
- \(Re\): Reynolds number
- \(R_h\): relative humidity, %
- \(Sc\): Schmidt number
- \(Sh\): Sherwood number
- \(t\): time, s
- \(T_{air}\): air temperature, °C
- \(T_L\): liquid temperature, °C
- \(TAN\): total ammonia nitrogen concentration, g/l as nitrogen
- \(TAN_{L,0}\): initial total ammonia nitrogen concentration, g/l as nitrogen
- \(U_{air}\): air velocity above the liquid, m/s
- \(\Sigma_{air}v_i\): sum of the atomic diffusion volumes of all elements in ammonia
- \(\Sigma_{air}v_i\): diffusion volume of air
- \(\alpha\): ratio of unionized concentration of ammonia to total ammonia nitrogen concentration in the liquid
- \(\mu_{air}\): air viscosity, kg/m s
- \(\rho_{air}\): air density, kg/m\(^3\)

### Superscripts

- \(a, b, c, n\): exponents
the two-film concept has not only been used extensively to calculate $K_{OL}$ for ammonia,\textsuperscript{4,6,11} but also the mass transfer rates for other volatile compounds.\textsuperscript{12-16}

2.2. Development of mass transfer coefficient correlations

A review\textsuperscript{4} of the existing mass transfer correlations for ammonia showed that ammonia volatilization is commonly correlated to air velocity and liquid temperature. In these correlations the influence of either one or a combination of the two factors on the mass transfer coefficient of ammonia was considered. However, other factors such as air temperature and the system geometry, which may also influence the volatilization of ammonia or any other gas were not considered.

To include the influence of system geometry and other air and liquid manure properties in the mass transfer coefficient correlations, the dimensionless number approach was used in this study. The advantage of using dimensionless numbers and groups is that, once they are defined, they can be used for any scale of the system. The common dimensionless numbers that have been used in mass transfer correlations include the Sherwood Sh, Schmidt Sc, and Reynolds Re numbers.\textsuperscript{16} These dimensionless numbers are normally related as:\textsuperscript{16}

$$Sh = C_K (Re)^a (Sc)^b$$

(2)

where $C_K$ is a constant and $a, b$ are exponents. In general, the Sherwood number contains the mass transfer coefficient, characteristic length, and the diffusionity terms. Reynolds number contains the velocity, characteristic length, density, and the viscosity terms. Schmidt number contains viscosity, density, and the diffusionity terms.

Using the information above and the fact that the resistance to ammonia volatilization from a liquid is primarily controlled by the gas phase,\textsuperscript{12} the mass transfer coefficient of ammonia, $K_{OL}$, was correlated to air density $\rho_{air}$, air viscosity $\mu_{air}$, air velocity $U_{air}$, ammonia diffusivity in air $D_{A-air}$, air temperature $T_{air}$, liquid manure temperature $T_L$, and the characteristic length $L$, of the emission chamber. The overall mass transfer coefficient $K_{OL}$ can be expressed as a function of these factors as

$$K_{OL} \propto f(\mu_{air}, \rho_{air}, D_{A-air}, U_{air}, T_{L}, T_{air}, L)$$

(3)

Using the dimensionless analysis procedure, a mathematical relationship defined by Eqn (4) was developed:\textsuperscript{17}

$$K_{OL} L = C_K \left( \frac{U_{air} L \rho_{air}}{\mu_{air}} \right)^a \left( \frac{\mu_{air}}{\rho_{air} D_{A-air}} \right)^b \left( \frac{T_{air}}{T_L} \right)^c$$

(4)

Four dimensionless numbers are included in Eqn (4). The dimensionless numbers are, from left to right Sherwood, Reynolds, Schmidt, and a temperature ratio, respectively. The main challenge in the correlation equation, Eqn (4), is to determine the constant $C_K$, and the exponents $a$, $b$, and $c$.

The air viscosity $\mu_{air}$, air density $\rho_{air}$, and ammonia diffusivity $D_{A-air}$, are calculated using the established empirical equations that are directly related to measurable environmental parameters such as air temperature, pressure, and relative humidity and molecular properties such as molecular weight and molecular diffusion volume. Equations (5) and (6) are used to calculate air viscosity and density, respectively.\textsuperscript{18}

$$\mu_{air} = 0.3768 \times 10^{-6} (273.15 + T_{air})^{0.683}$$

(5)

$$\rho_{air} = \left( \frac{353}{273.15 + T_{air}} \right) \frac{(760 - 0.3783) (R_h) e^{0.0596 T_{air} + 1666}}{760}$$

(6)

where $R_h$ is the relative humidity. Diffusivity of ammonia is calculated using Eqn (7) developed by Fuller et al.\textsuperscript{19}

$$D_{A-air} = \frac{10^{-7} (273.15 + T_{air})^{1.75} (1/M_A + 1/M_{air})^{1/2}}{P \left[ (\sum_{i} v_i)^{1/3} + (\sum_{i} v_i)^{1/3} \right]^2}$$

(7)

where $M_A$ is the molecular weight of ammonia in g/mol, $M_{air}$, the molecular weight of air in g/mol, $P$ is the atmospheric pressure in atm, $\sum_{i} v_i$ is the sum of all atomic diffusion volumes of the elements in ammonia, and $\sum_{air} v_i$ is the diffusion volume of air.

3. Experimental methods for determining ammonia mass transfer coefficient

Equation (1) provides a basis to determine the mass transfer coefficient of ammonia from an aqueous solution or liquid manure. Assuming that ammonia concentration in the liquid manure or the aqueous solution is uniform, Eqn (1) can be written to express the mass transfer rate of total ammonia as shown in Eqn (8) for a given liquid volume $V$ and surface area $A_s$:

$$\frac{dM_{TAN}}{dt} = K_{OL} A_s ([NH_3]_L - [NH_3]_{air})$$

(8)

where $M_{TAN}$ is the mass of total ammonia in a given volume of liquid in kg, $K_{OL}$ is the overall mass transfer of ammonia in m/s, $[NH_3]_L$ is the free ammonia concentration in solution in g/l, and $[NH_3]_{air}$ is the free ammonia concentration in the air in g/l.

However, Eqn (1) cannot be used as it is because direct measurement of $[NH_3]_L$ is not possible. With the knowledge of ammonia chemistry in aqueous solutions,\textsuperscript{14,11,20} however, $[NH_3]_L$ can be obtained from total ammonia nitrogen concentration which can be measured directly.
Total ammonia nitrogen $TAN$ is defined as the sum of the concentrations of all ammonia species in solution

$$TAN = [NH_3]_L + [NH_4^+]$$  \hspace{1cm} (9)

where $[NH_4^+]$ is the ammonium ion concentration in g/l.

The partitioning and concentrations of ammonia species in a solution depends on pH. The concentration of each ammonia species in a solution can be expressed as a fraction of $TAN$ using their respective ionization fractions. Using this concept, the concentration of molecular ammonia can be calculated as

$$[NH_3]_L = x \times TAN$$  \hspace{1cm} (10)

where $x$ is the ratio of unionized concentration of ammonia to the total ammonia nitrogen concentration in the liquid.

Assuming that ammonia concentration in the air is negligible, i.e., $[NH_3]_{air} = 0$, ammonia loss is caused by the volatilization process only, and that the total ammonia concentration in a sample is equal to the product of the total ammonia concentration and the volume of the sample, i.e., $M_{TAN} = V \times TAN$, Eqn (8) can be transformed into the following differential equation:

$$\frac{d(TAN)}{dt} = K_{OL} \frac{A_o}{V} [NH_3]_L$$  \hspace{1cm} (11)

Substituting Eqn (10) into Eqn (11) and integrating, gives an expression that relates the total ammonia concentration to time:

$$TAN = TAN_{L,0} e^{\frac{K_{OL}}{x} (\frac{A_o}{V}) t}$$  \hspace{1cm} (12)

Equation (12) was used to determine $K_{OL}$ values experimentally by measuring the initial total ammonia concentration at time zero, and the residual total ammonia concentrations at specific time intervals over a period of time $t$ during each experiment. The total ammonia concentration data were fitted to a logarithmic transformation of Eqn (12), and then a linear regression was performed to determine $K_{OL}$ for each test condition using time $t$ as the independent variable, and total ammonia concentration as the dependent variable. The overall mass transfer coefficient $K_{OL}$ for ammonia for every test condition was calculated from the slope of the regression line.

### 3.1. Experimental procedure

The experiments were conducted in a convective emission chamber (CEC) where air temperature, velocity, turbulence levels, and relative humidity were precisely controlled.\(^{21}\) The overall dimensions of the CEC were $60 \times 47 \times 0.15$ m and consisted of a clean air generation unit, an air conditioning and flow control unit, turbulence generation screens, and a test chamber. The test chamber (Fig. 1) was made of plexiglas with dimensions $12 \times 4 \times 0.15$ m. At the bottom of the test chamber a $27.3 \times 17.8 \times 3.5$ cm pan was used to hold liquid samples for test. The pan was fitted with a water jacket around it to control the liquid sample temperature by circulating water at appropriate temperatures from a refrigerated/heated water bath. Two pieces of metal screens with 3-mm diameter openings were installed 10 cm apart at the inlet of the test chamber to provide uniform air velocity over the liquid surface.

The air velocities used for the experiment ranged from 0.1 to 0.5 m/s, while the air and liquid temperature range

<table>
<thead>
<tr>
<th>Test run</th>
<th>Air temperature $(T_{air})$, °C</th>
<th>Air velocity $(U_{air})$, m/s</th>
<th>Liquid temperature $(T_L)$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>0.1</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>0.2</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>0.3</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>0.4</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>0.5</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>20</td>
<td>0.3</td>
<td>15</td>
</tr>
<tr>
<td>7</td>
<td>20</td>
<td>0.3</td>
<td>20</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>0.3</td>
<td>30</td>
</tr>
<tr>
<td>9</td>
<td>30</td>
<td>0.3</td>
<td>35</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
<td>0.3</td>
<td>20</td>
</tr>
<tr>
<td>11</td>
<td>25</td>
<td>0.3</td>
<td>20</td>
</tr>
<tr>
<td>12</td>
<td>30</td>
<td>0.3</td>
<td>20</td>
</tr>
<tr>
<td>13</td>
<td>35</td>
<td>0.3</td>
<td>20</td>
</tr>
</tbody>
</table>
was 15–35°C. The temperatures and air velocities used were chosen to include typical conditions found in environmentally controlled swine buildings. The experimental plan used in this study is outlined in Table 1. The experimental plan was used for both the aqueous solution and liquid manure. Ammonia volatilization from each of the two solutions was tested separately for every test condition listed. Each test lasted 4 h and was replicated twice.

Liquid samples (1500 ml) for every test were prepared by diluting 30% ammonium hydroxide (NH₄OH) solution either with tap water for the aqueous solution or partially digested liquid swine manure, to make a solution with an initial TAN concentration of approximately 4000 mg-N/l. The pH of each test solution was then adjusted to 12 using 10 M NaOH solution. The manure used in this study was collected from the finishing building of the Swine Research Farm at the University of Illinois at Urbana-Champaign. The manure was settled (and the top layer used after being digested for a period of 30 days) as described by Zhang. The digested manure had on average a total solids content < 1% and 2000 mg/l TAN.

Before any test was done, the CEC was operated for at least 1 h to allow the air temperature, velocity, and relative humidity to stabilize. The air velocity and temperature were measured by a hot wire probe, model 8330 manufactured by TSI Inc., while the relative humidity was measured by a psychrometer model 784 made by VISTA Scientific. After the CEC stabilized, 1400 ml of the test solution was placed in the sample pan. The CEC was run for an additional 30 min to let the surface and the bulk of the liquid sample equilibrate to the testing conditions before making any measurement. Once the tests conditions were achieved, samples were taken every 30 min from the surface layer (2 mm below the open liquid surface) of the test solution using a pipette for TAN measurements. The TAN concentration was determined using the ammonia-selective electrode method described in the Standard Methods for the Examination of Water and Wastewater. An ammonia ion selective probe, Model 95-12 made by Orion Research Incorporated Laboratory, was used in this procedure.

4. Results and discussion

An example of the result for the total ammonia concentration decay from liquid manure for a set of conditions tested (air temperature of 20°C, air velocity of 0.3 m/s, and liquid temperatures of 15, 20, 25, 30 and 35°C) is shown in Fig. 2. The ammonia concentration in the liquid decreased exponentially as governed by Eqn (12). The effects of air velocity, liquid temperature, air temperature, and solids content on the mass transfer coefficient are described as follows.

![Fig. 2. Typical ammonia concentration decay curves expressed as a ratio of total ammonia nitrogen TAN at time t to the initial total ammonia nitrogen concentration TAN₀ for ammonia volatilization from liquid manure for different liquid manure temperatures (15, 20, 25, 30, and 35°C) and constant air temperature (20°C) and air velocity (0.3 m/s): ⋆, 15°C; ■, 20°C; ●, 25°C; Δ, 30°C; ×, 35°C.](image)

4.1. Effect of air velocity on mass transfer coefficient

Figure 3 shows the experimental mass transfer coefficient of ammonia at different air velocities and constant air and liquid temperatures of 20°C. The mass transfer coefficient increased as the air velocity increased. Generally, this is the expected result for soluble gases such as ammonia and organic solutes whose volatilizations are controlled mainly by the gas film. Air velocity has the effect of reducing the boundary layer thickness over the liquid surface. As the velocity increases, the turbulence intensity also increases resulting in a thinner boundary layer formed at the interface. The smaller the boundary layer, the lower the resistance to the volatilization process, thereby leading to a bigger mass transfer coefficient and mass transfer rate.

![Fig. 3. Mass transfer coefficient for ammonia volatilization from liquid manure and aqueous solution for different air velocities and constant air and liquid temperatures (20°C): ⋆, water; ■, manure.](image)
4.2. **Effect of liquid and air temperatures on mass transfer coefficient**

The effects of liquid temperature on the mass transfer coefficient of ammonia are presented in Fig. 4. Mass transfer coefficient increased as the liquid temperature was increased. Fundamentally, temperature influences most physical properties (viscosity, density and mass diffusivity) of the liquid that govern the dispersion of a solute in a liquid. An increase in liquid temperature lowers the viscosity and the density of the liquid but increases the diffusivity of the solute in the liquid. When the diffusivity of the solute increases, there is a corresponding increase in mass transfer rate, which implicitly implies an increase in mass transfer coefficient. Also, in theory, an increase in liquid temperature will cause a high equilibrium dissociation constant and a lower solubility of ammonia in the water, which results in higher ammonia volatilization rates.

**Figure 5** shows the results for the effect of different air temperatures on the mass transfer coefficient of ammonia. Generally, the magnitude of the mass transfer coefficient decreased as the air temperature was increased.

The effect of liquid and air temperature difference on the mass transfer coefficient of ammonia is presented in Fig. 6. Larger liquid–air temperature differences, i.e., where the liquid temperatures were higher than the air temperatures, resulted in bigger mass transfer coefficient. This could possibly be explained by the fact that at higher liquid temperature the air immediately above the liquid surface warms up and becomes lighter. This may result in some turbulence induced by thermal and density buoyancy. The turbulence caused may result in a reduced resistance to mass flow from the liquid by reducing the boundary layer thickness. The turbulence could also enhance the removal of ammonia from above the liquid surface. These effects could result in an increase in the mass transfer rate across the liquid surface layer, thereby increasing the magnitude of the mass transfer coefficient with increasing liquid–air temperature difference.

4.3. **Effect of solids content on mass transfer coefficient**

The influence of manure solids content on the mass transfer coefficient of ammonia was determined by comparing the values obtained from the same test conditions (air velocity, air temperature, and liquid temperature) for liquid manure and aqueous solution. A paired t-test comparison was done at 5% significance level. All the p-values were greater than the critical value of 0.05. This
suggests that the presence of solids ( < 1%) in liquid manure had no statistically significant effect on the mass transfer coefficient for ammonia with respect to air velocity, air temperature, and liquid temperature. However, since solids in liquid manure or aqueous solutions could affect both the solubility and the mass transfer coefficient of ammonia, it is apparent that the experimental method used in this study was not able to differentiate between these effects.

4.4. Mass transfer coefficient correlations

The mass transfer coefficient was correlated to the liquid properties and environmental conditions according to Eqn (4). The major challenge in Eqn (4) was to calculate or determine the constants and the exponents. Exponents $a$ and $c$ were determined by regression analysis using the experimental data where the air velocity and liquid temperature were varied, respectively, while the other experimental factors were kept constant. The scheme used for exponents $a$ and $c$ could not be used for exponent $b$ because both Reynolds and Schmidt numbers are functions of air temperature. A method where an arbitrary number is assigned to the unknown exponent was used. This method has been used frequently in other similar applications. The assignment was based on the fact that mass transfer coefficient $K$ of a compound is proportional to the molecular diffusion $D$ of the compound raised to some power as shown in Eqn (13):\[ K \propto D^n \] (13)

Values of the exponent $n$ ranging from 0.15 to 1.0 are reported for several studies on gas–liquid interface mass transfer. The most commonly used numbers are 1/2, 2/3, or 1, with no specific reason given to justify the assignments. For this study, an average value of exponent $n = 0.575$ was used in the correlations. Exponent $b$ was calculated by rearranging Eqn (4) into a form similar to Eqn (13) and the resulting exponents of $D$ equated. The results for the constants and the exponents in Eqn (4) are reported in Table 2.

Using these values, Eqn (4) can be rewritten to express the overall mass transfer coefficient for ammonia volatilization from aqueous solutions as,

\[
K_{OL} = 3.12 \frac{D_{a}^{0.58} \rho_{air}^{0.31} U_{air}^{0.12} T_{air}^{0.77}}{L^{0.88} \rho_{air}^{0.31} T_{air}^{0.77}} \] (14)

and for ammonia volatilization from liquid manure as

\[
K_{OL} = 3.70 \frac{D_{a}^{0.58} \rho_{air}^{0.33} U_{air}^{0.10} T_{air}^{0.97}}{L^{0.60} \rho_{air}^{0.33} T_{air}^{0.97}} \] (15)

Table 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_k$</td>
<td>3.12</td>
</tr>
<tr>
<td>$a$</td>
<td>0.12</td>
</tr>
<tr>
<td>$b$</td>
<td>0.53</td>
</tr>
<tr>
<td>$c$</td>
<td>-0.77</td>
</tr>
</tbody>
</table>

Aqueous solution | Liquid manure

4.5. Predicted mass transfer coefficient

Using Eqn (15), the values of mass transfer coefficient of ammonia for liquid manure were calculated and plotted against the air velocity for various liquid manure and air temperatures (Figs 7 and 8). The mass transfer coefficient for ammonia was calculated for air velocity up to 0.6 m/s. The mass transfer coefficient increases as air velocity increases for both air and liquid manure temperatures. The correlation equation predicts that the mass transfer coefficient increases with liquid temperature (Fig. 7), but decreases as the air temperature increases (Fig. 8).

The influences of extreme and moderate temperature combinations on the mass transfer coefficient of ammonia are presented in Fig. 9. The results show that a combination of lower air temperatures (15°C) and higher liquid temperatures (35°C) is more likely to result in a larger mass transfer coefficient compared to other temperature combinations. On the other hand, higher air temperature (35°C) and lower liquid temperature (15°C) combination would result in lower mass transfer coefficients at different air velocities. Thus, it can be concluded that reduced ammonia volatilization from liquid swine...
manure may be effectively obtained by reducing the liquid manure temperatures and providing low air velocities and warm air temperatures in a storage pit.

4.6. Sensitivity analysis

A sensitivity analysis was done to determine the relative changes in the overall mass transfer coefficient of ammonia from liquid to air with respect to changes in air velocity, liquid temperature, and air temperature. Absolute sensitivity coefficients were calculated for different air velocity, air temperature, and liquid temperature ranges as outlined by Haan. The results are presented in Tables 3 and 4. The change in mass transfer coefficient per unit change of air velocity was higher than the changes caused by unit changes in air and liquid temperatures. However, it is difficult to make absolute comparisons because the variables have different units. A sensitivity analysis was also performed to determine how the mass transfer coefficient changes at different air temperature, air velocity, and liquid temperature ranges. The results show that at the lower air velocity range, 0.1–0.2 m/s, the mass transfer coefficient is more sensitive to velocity changes compared to the higher velocity ranges, 0.2–0.3 m/s. Similarly, for both air and liquid temperatures, the mass transfer coefficient is more sensitive to temperature changes in the lower, 15–20°C, compared to the higher, 30–35°C, temperature ranges.

5. Conclusion

A correlation for the overall mass transfer coefficient of ammonia with liquid properties and environmental conditions was developed for ammonia volatilizing from aqueous solutions as well as from liquid manure in a convective emission chamber where the air velocity, temperature, turbulence, and relative humidity were precisely controlled. The latter correlation was then used to calculate the mass transfer coefficient of ammonia in liquid swine manure for different air velocity, air temperature, and liquid temperature combinations. The mass transfer coefficient was observed to increase with increasing air velocity and liquid temperature but decreased with increasing air temperature. Analysis of air-liquid temperature combinations on the influence of mass transfer coefficient showed that low air temperature (15°C) and high liquid temperature (35°C) combination is more likely to result in higher ammonia volatilization rates compared to other temperature combinations. On the other hand, higher air temperature (35°C) and lower

<table>
<thead>
<tr>
<th>Air velocity range, m/s</th>
<th>Sensitivity</th>
<th>Manure temperature range, °C</th>
<th>Sensitivity, m/s °C</th>
<th>Air temperature range, °C</th>
<th>Sensitivity, m/s °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1–0.2</td>
<td>6.68 × 10⁻⁵</td>
<td>15–20</td>
<td>5.38 × 10⁻⁶</td>
<td>15–20</td>
<td>-6.97 × 10⁻⁶</td>
</tr>
<tr>
<td>0.2–0.3</td>
<td>4.27 × 10⁻⁵</td>
<td>20–25</td>
<td>5.34 × 10⁻⁶</td>
<td>20–25</td>
<td>-4.25 × 10⁻⁶</td>
</tr>
<tr>
<td>0.3–0.4</td>
<td>3.16 × 10⁻⁵</td>
<td>25–30</td>
<td>5.31 × 10⁻⁶</td>
<td>25–30</td>
<td>-2.86 × 10⁻⁶</td>
</tr>
<tr>
<td>0.4–0.5</td>
<td>2.16 × 10⁻⁵</td>
<td>30–35</td>
<td>5.28 × 10⁻⁶</td>
<td>30–35</td>
<td>-2.06 × 10⁻⁶</td>
</tr>
</tbody>
</table>
liquid temperature (15°C) combination would result in lower ammonia volatilization rates at different air velocities.

The mass transfer coefficient for ammonia was much more sensitive to changes in air velocity in the lower compared to the higher velocity ranges. Similar sensitivity responses were obtained for both air and liquid temperature ranges.

Acknowledgements

This research was supported by the National Institute of Occupational Safety and Health (NIOSH) through the National Farm Medicine Center, Marshfield Wisconsin.

References

1 Donham K J; Yeggy J; Dague R R Production rates of toxic gases from liquid swine manure: health implications for workers and animals in swine confinement buildings. Biological Wastes, 1988, 24, 161–173
4 Zhang R H Degradation of swine manure and a computer model for predicting the desorption rate of ammonia from an under-floor pit. PhD dissertation. Library, University of Illinois, Urbana, IL, 1992
5 Bliss P J; Jiang K; Schulz T J The development of a sampling system for the determination of odor emission rates from areal surfaces, Part II: mathematical model. Journal of Air and Waste Management Association, 1995, 45, 989–994
7 Schulte D D; DeShazer J A; Ifeadi C N Effect of slotted floors on air-flow characteristics in a model swine confinement building. Transactions of the American Society of Agricultural Engineers, 1972, 32, 947–950
8 De Praetere K; Van Der Biest W Airflow patterns in piggery with fully slatted floors and their effect on ammonia distribution. Journal of Agricultural Engineering Research, 1990, 46, 31–44
10 Lewis W K; Whitman W G Principles of gas absorption. Industrial and Engineering Chemistry, 1924, 16(12), 1215–1220
11 Srinath E G; Loehr R C Ammonia desorption by diffused aeration. Journal of Water Pollution Control Federation, 1974, 46(8), 1939–1957
12 Halsam R T; Hersey R L; Keen R H Effect of gas velocity and temperature on rate of absorption. Industrial and Engineering Chemistry, 1924, 16(12), 1224–1230
13 Cohen Y; Coccio W; Mackay D Laboratory study of liquid-phase controlled volatilization rates in the presence of wind waves. Environmental Science and Technology, 1978, 12(5), 553–558
14 Smith J H; Bomberger D C Jr.; Haynes D L Prediction of the volatilization rates of high volatility chemicals from natural water bodies. Environmental Science and Technology, 1980, 14(11), 1332–1337
15 Mihelcic J R; Baillod C R; Crittenden J C Estimation of VOC emissions from wastewater facilities by volatilization and stripping. Journal of Air and Waste Management Association, 1993, 43, 97–105
21 Shaw B W Use of a convective emission chamber to study particle re-suspension. PhD dissertation. Library, University of Illinois, Urbana, IL, 1994
23 Mackay D; Yeun T K Mass transfer coefficient correlations for volatilization of organic solutes from water. Environmental Science and Technology, 1983, 17(4), 211–217

26 Hichri H; Accary A; Puaux J P; Andrieu J Gas–liquid mass transfer coefficients in a slurry batch reactor equipped with a self-gas inducing agitator. Industrial and Engineering Chemistry Research, 1992, 31(8), 1864–1867


28 Munz C; Roberts P V Gas and liquid phase mass transfer resistance’s of organic compounds during mechanical surface aeration. Water Resources, 1989, 23(5), 589–601

29 Haan C T Evaluation of uncertainty in hydrologic and water quality models. A tutorial presentation at the ASAE Annual International Meeting, Chicago, IL, 22 June, 1995