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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

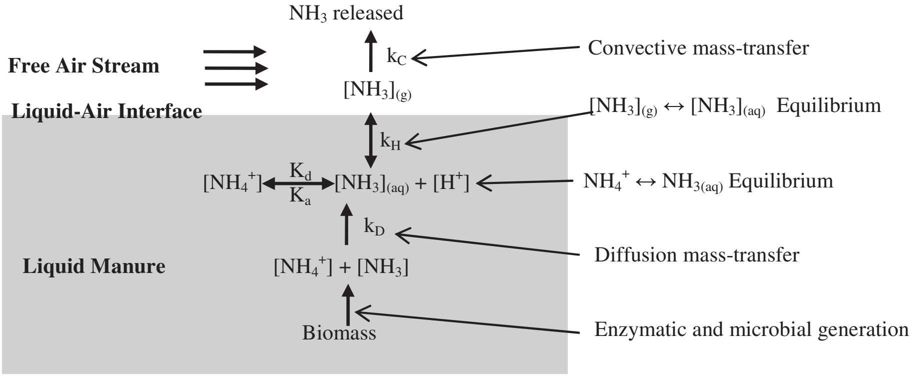

Fig. 1. Ammonia release mechanism from liquid manure (Ni, 1999).