IMPACT OF ANAEROBIC DIGESTION OF LIQUID DAIRY MANURE ON AMMONIA VOLATILIZATION PROCESS

K. Koirala, P. M. Ndegwa, H. S. Joo, C. Frear, C. O. Stockle, J. H. Harrison

ABSTRACT. *The goal of this study was to determine the effect of anaerobic digestion (AD) on ammonia volatilization from liquid dairy manure, in storage or treatment lagoon, prior to land application. Physical and chemical properties of liquid dairy manure, which may affect ammonia volatilization, were determined before and after AD. The properties of interest included particle size distribution (PSD), total solids (TS), volatile solids (VS), viscosity, pH, total ammoniacal nitrogen (TAN), and ionic strength (IS). The overall mass transfer coefficient of ammonia (K_{oL}) and the NH_3 fraction of TAN (β) for the undigested (UD) and AD manures were then experimentally determined in a laboratory convective emission chamber (CEC) at a constant wind speed of 1.5 m s^{-1} and fixed air temperature of 25°C at manure temperatures of 15°C, 25°C, and 35°C. The PSD indicated non-normal left-skewed distributions for both AD and UD manures particles, suggestive of heavier concentrations of particles toward the lower particle size range. The volume median diameters (VMD) for solids from UD and AD were not significantly different (p= 0.65), but the geometric standard deviations (GSD) were significantly different (p = 0.001), indicating slightly larger particles but more widely distributed solids in UD manure than in AD manure. Results also indicated significantly higher pH, TAN, ionic strength (IS), and viscosity in AD manure. The β for AD manure, determined under identical conditions (air temperature, liquid temperature, and airflow), was significantly higher (p < 0.001) than for UD manure. However, mass transfer of ammonia (K_{oL}) was significantly lower for AD manure than for UD manure (p < 0.001). Overall, these findings suggest that AD of dairy manure significantly increased initial ammonia volatilization potential from liquid dairy manure, with the largest increase (~61%) emanating from increased ammonium dissociation. The initial flux of ammonia, at 15°C, was ~16% more from AD manure than from UD manure.*

Keywords. *Ammonium dissociation, Mass transfer coefficient, Process-based models, TAN ammonia fraction (β).*

Advanced manure treatment systems, such as aerobic and anaerobic digestion, are essential for mitigation of odor and other gaseous emissions from livestock operations (Laboski et al., 2010; Whelan et al., 2010). These treatment techniques impact the physical and chemical properties of the manure in different ways, which may then either positively or adversely impact individual emissions. Significant reductions of total solids (TS) and volatile solids (VS) from anaerobic digestion (AD) of livestock manure, for instance, have been reported in past studies (Adelekan et al., 2010; Sakar et al., 2009; Zhang et al., 2008). Other studies have reported significant changes in pH and TAN after AD of livestock manure (Adelekan et al., 2010; Wang et al., 2010; Sakar et al., 2009; Van Velsen, 1977; Sommer and Husted, 1995; Azevedo and Stout, 1974). The focus of this study was to evaluate the influence of AD and subsequent physical and chemical changes on the potential for ammonia volatilization from liquid dairy manure.

Process-based emission models provide insights into the core mechanisms governing emission rates from bulk manure using pertinent manure, environmental, and meteorological parameters. A generic model of ammonia emission from bulk liquid livestock manure is presented in equation 1 (Ni, 1999; Liang et al., 2002; Arogo et al., 1999). In principle, $[NH_3]_L >> [NH_3]_a$, and its effect is negligible in this process, which reduces equation 1 to equation 2. To determine ammonia flux using equation 2 for a given exposed surface area (A), both K_{oL} and $[NH_3]_L$ need to be known, which presents a problem, as it is not possible to directly measure $[NH_3]_L$ in liquid or solution. However, the dissociation constant (K_d) of ammonium ions (NH_4^+) defines the fraction of $[NH_3]_L$ (β) with respect to measurable TAN concentration in liquid or solution according to equation 3 (Vaddella, et al., 2011; Arogo et al., 2003). Combining equations 2 and 3 results in equation 4, which can be used to estimate ammonia flux from bulk liquid livestock manure when K_{oL}, K_d, or β, and $[TAN]_L$ are known or are determinable. This equation can also be used to quantify the effect of any manure treatment on the process of ammonia volatilization. Equation 4 describes a dynamic model in the sense that the concentration of TAN decreases with time. However, the model is sufficient to evaluate the effect of any manure treatment at initial conditions, i.e.,

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The authors are **Kedar Koirala, ASABE Member,** Graduate Student, **Pius M. Ndegwa, ASABE Member,** Associate Professor, **Hung Soo Joo,** Postdoctoral Fellow, **Craig Frear,** Assistant Research Professor, and **Claudio O. Stockle, ASABE Member,** Professor, Department of Biological Systems Engineering, Washington State University, Pullman, Washington; **Joseph H. Harrison, ASABE Member,** Professor, Department of Animal Science, Washington State University, Puyallup, Washington. **Corresponding author:** Pius M. Ndegwa, P.O. Box 646120, Washington State University, Pullman, WA 99164-6120; phone: 509-335-8167; e-mail: ndegwa@wsu.edu.

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immediately before and after the treatment in question:

$$Q = K_{oL} \cdot \left([\mathrm{NH_3}]_L - [\mathrm{NH_3}]_a \right) \tag{1}$$

$$Q = K_{oL} \cdot [\mathrm{NH_3}]_L \tag{2}$$

$$[\mathrm{NH_3}]_L = \beta \cdot [\mathrm{TAN}]_L \tag{3}$$

$$Q = K_{oL} \cdot \beta \cdot [\mathrm{TAN}]_L \tag{4}$$

where Q is the ammonia flux (g m^{-2} s^{-1}), K_{oL} is the overall mass transfer coefficient (m s^{-1}), $[NH_3]_L$ and $[NH_3]_a$ are the respective concentrations of ammonia at the liquid-air interface and in the free air stream (g m^{-3}), TAN is the total ammoniacal nitrogen in (g m^{-3}), and β is the fraction of $[NH_3]_L$ with respect to TAN.

Past studies have shown that physical and chemical properties including TS, viscosity, pH, TAN, and ionic strength (IS) affect the ammonia volatilization process (Sommer et al., 1991; Olesen and Sommer, 1993; Chaoui et al., 2009; Mashad et al., 2005; Vaddella et al., 2011). Several studies have revealed an inverse relationship between ammonia volatilization and TS concentration in liquid manure (Vaddella et al., 2011; Liang et al., 2002; Zhang, 1992; Hashimoto and Ludington, 1971). Viscosity has been observed to increase after AD of dairy manure, which ultimately may impede ammonia volatilization from stored AD effluent. Ortenblad (2000) reported higher viscosity in AD manure compared to undigested (UD) manure. During anaerobic processing, organic nitrogen converts to inorganic nitrogen, increasing the pH and TAN concentration. In general, increases in TAN concentration and pH result in increased ammonia emission from stored AD effluent (Sommer et al., 1991; Olesen and Sommer, 1993). The concentration of ions (cations and anions) in solution is referred to as ionic strength (IS) and is important for determining the activities of individual ions (Snoeyink and Jenkins, 1980). Normally, an increase in IS results in a decreased activity coefficient, which in turn decreases the ammonium dissociation in the manure solution (Arogo et al., 2003; Montes et al., 2009) and the fraction of $NH_{3(aq)}$ in the liquid manure.

The overall goal of this study was to quantify the effect of AD on the ammonia volatilization process. Although the physical and chemical changes of manure are useful as qualitative predictors of ammonia volatilization, they are insufficient for quantifying the net effect of the anaerobic treatment on this process with respect to livestock manures. However, the process model expressed in equation 4 can sufficiently quantify the net effect on the ammonia volatilization process. Therefore, the specific objectives of this study were to: (1) study the physical and chemical changes in liquid dairy manure during AD in order to elucidate their respective roles in this process, and (2) determine their net effect on key manure parameters (K_{oL}, β, and TAN) governing the ammonia emission process, as expressed in equation 4.

Table 1. Feed ration composition (%) at the dairy from which manure was sampled during the four weeks prior to the sampling date (24 April 2012).

	Composition (%) by Date (2012)		
Ingredient	27 March	12 April	20 April
Corn silage	43.6	43.5	46.8
MC Grain Mix[a]	29.1	29.0	26.6
Rumen bypass fat	0.5	0.3	0.3
Hay	8.9	9.4	9.2
Haylage (alfalfa)	14.4	14.4	14.0
Haylage Sudan	3.4	3.4	3.1
Total	100.0	100.0	100.0

[a] The ingredients in the MC Grain Mix did not change.

Material and Methods

Manure Collection

The manure samples for this study were sourced from a commercial flush dairy located in Outlook, Washington, operating a mixed plug-flow mesophilic anaerobic digester (DVO, Inc., Chilton, Wisc.). Samples of raw liquid dairy manure were collected in 20 L sealable plastic buckets from the manure receiving tank. Similarly, samples of anaerobically digested manure were collected from the digester effluent tank. The AD and UD manure samples were both collected as single batches to run the entire study. The samples were transported to the laboratory and stored in a cold room at 5°C until commencement of studies and analysis. The composition of the feed rations at this dairy, dating four weeks prior to the manure sampling date, are presented in table 1. There were no significant variations in the feed rations during this period. Since the retention time of the digester influent averaged 21 d, the differences in the AD and UD manures were thus attributed to the digestion process.

Determination of Particle Size Distribution

Particle size distribution (PSD) of the UD and AD manure was determined using a Mastersizer (model MS2000, Malvern Instruments, Westborough, Mass.). The Mastersizer uses laser diffraction of particles in liquid suspension and places the particles in 64 different size classes based on percent volume. The particle suspensions were then placed in a stirred-tank and circulated through the cell placed in the path of the laser beam. Both UD and AD samples were run as multiple subsamples until replicate values for fine (0.01 to 2.1 μm), medium (2.2 to 52 μm), and coarse (>52 μm) particles categories were within 5% to 10%. The samples were introduced into a sample mixing chamber until the obscuration factor was 15% to 25% (10% to 30% is the acceptable range according to the manufacturer's instructions). The particles were then circulated through the instrument until a stable signal was reached, completing the PSD analysis. The vigor of mixing should be balanced so that dispersion occurs without undue breakage of individual particles. Both UD and AD samples were treated in a similar manner during the entire process to minimize process variability. In general, laser diffraction results are reported on a volume basis, so volume mean diameters and geometric standard deviations are reported.

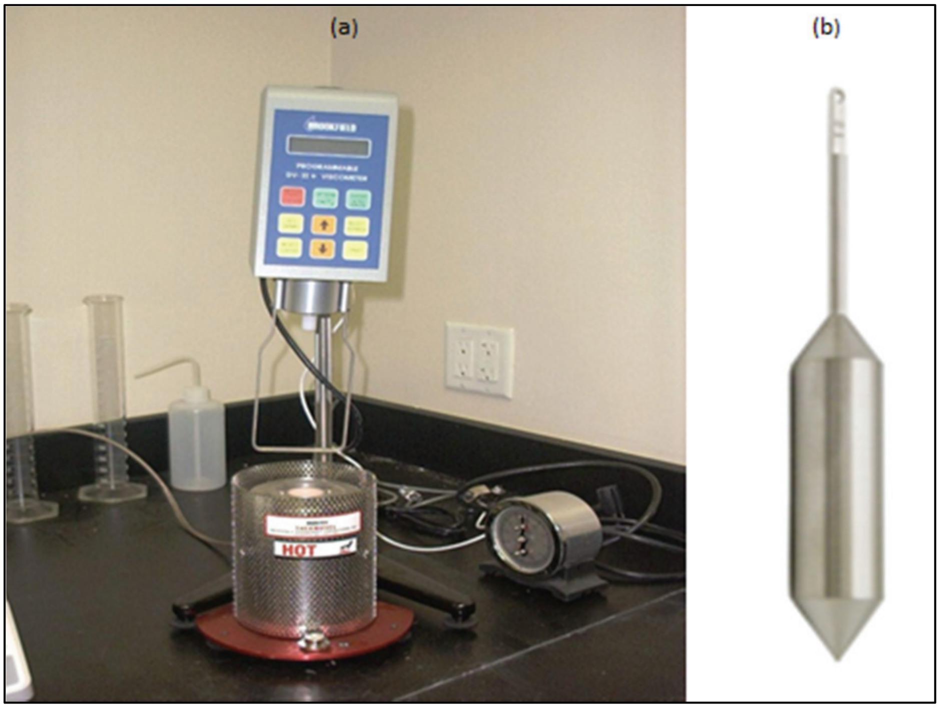

Figure 1. Viscosity measurement apparatus: (a) Brookfield DV-II+ Pro viscometer, and (b) spindle.

Analyses of Other Manure Properties

Total solids (TS) and volatile solids (VS) of AD and UD manures were determined following Standard Methods (APHA, 2005). The pH of liquid manure was measured using a standard pH meter (model 900A, Orion Research, Inc., Boston, Mass.). Concentration of TAN was determined following Standard Methods (APHA, 1995). Electrical conductivity (EC) was measured just before the experiments using an EC meter (model SG7-FK2, SevenGo conductivity meters, Mettler Toledo, Columbus, Ohio). The EC values were converted to ionic strength (mol L^{-1}) using an established EC-ionic strength relationship (Snoeyink and Jenkins, 1980). Viscosity measurements were performed using a viscometer (model DV-II+ Pro, Brookfield Engineering Laboratories, Inc., Middleboro, Mass.) at a manure temperature of 45°C (fig. 1a). The most important procedures for viscosity measurement are the selection of an appropriate spindle (fig. 1b) and rotational speed (rpm) during the measurements. According to the manufacturer's instructions, viscosity measurements are acceptable within the torque range of 10% to 100% for any combination of spindle and rotational speed because of significant errors below the 10% torque range (Brookfield, 2013, pp. 16-18). For this study, a No. 21 spindle at a rotational speed of 100 rpm was found adequate because it operated within the prescribed torque range at a manure temperature of 45°C. Below this temperature, the torque was <10%, which was unacceptable.

Fraction of Un-ionized NH_3 and Overall Mass Transfer Coefficients

Ammonia volatilization studies were performed in a modular laboratory-scale convective emission chamber (CEC) adapted from previous research (Vaddella et al., 2013; Vaddella et al., 2011; Arogo et al., 1999; Shaw, 1994; Zhang, 1992). The CEC was started approximately 20 min prior to each experimental run to allow it to acclimate to specified conditions (i.e., airflow speed, air temperature, and water bath temperature). All experiments were performed at both the original manure pH and at a pH of 11.5, and at liquid temperatures of 15°C, 25°C, and 35°C. The pH of 11.5 was chosen because at pH of 11.0 and above, TAN is entirely comprised of un-ionized NH_3, or NH_4^+ ions are fully dissociated. As shown in the Data Analysis section that follows, this is important for computing both the mass transfer coefficients and the fraction of un-ionized ammonia at the pH of interest. For pH 11.5, a well-mixed 2.3 L manure sample at each temperature level was poured into a test pan, and the pH was adjusted to pH of 11.5 with NaOH solution. Airflow speed and air temperature were held constant at 1.5 m s^{-1} and 25°C for all experimental runs. To monitor ammonia volatilization, a 2.5 mL liquid sample was randomly taken from two locations within the pan using a pipette every 0.5 h for 3 h (i.e., t = 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 h). Simultaneous observations of airflow speed and liquid temperature were also recorded. Sampled liquids were immediately injected into 5 mL 0.2 M sulfuric acid in 15 mL test-tubes to stop ammonia volatilization, and the test-tubes were capped to avoid spillage of the samples. The collected samples were stored in a refrigerator at 4°C between collection and analysis of TAN concentration. In most cases, the samples were analyzed immediately after each experiment. Liquid manure temperature, pH, and electrical conductivity were also determined at the beginning and end of each experiment. Each test was conducted in duplicate.

DATA ANALYSIS

The K_{oL} was computed using equations 5 and 6 according to previous research (Vaddella et al., 2011; Arogo et al., 2003; Arogo et al., 1999). In particular, K_{oL} was computed from the slope of equation 5 with data obtained at pH 11.5 because $\beta \approx 1$ at pH $\geq$ 11.0 (Vaddella et al., 2011; Arogo et al., 2003; Arogo et al., 1999) and h is known. The fraction of NH_3 (β_{int}) at the original pH of manure (pH_{int}) was calculated by dividing the slope (s_{int}) of the linear regression between TAN and time (s_{int}) and the slope at pH of 11.5 where β is known (β = 1 at pH ≥ 11.0), as shown in equation 6:

$$\ln\left[\frac{\text{TAN}_t}{\text{TAN}_0}\right] = -K_{oL} \cdot \frac{\beta}{h} \cdot t \quad (5)$$

$$\frac{s_{int}}{s_{\text{pH}\geq 11}} = \frac{\beta_{int}}{\beta_{\text{pH}\geq 11}} = \beta_{int} \quad (6)$$

where [TAN_0] and [TAN_t] are the concentrations of TAN in the test liquid manure at time t = 0 and any other time t, β is the fraction of un-ionized NH_3 of TAN in liquid manure, h is the depth of liquid manure in the pan (m), s_{int} is the slope at the pH of interest, β_{int} is the fraction of un-ionized NH_3 at the unadjusted pH of the manure (pH_{int}).

In order to quantify the role of PSD on ammonia volatilization from liquid manure, it is necessary to evaluate the particles size characteristics of the manure solids. The volume median diameter (VMD) and the geometric standard deviation (GSD) fully characterize the PSD. A log-normal distribution was fitted to the PSD for UD and AD manure solids to accomplish this process. The VMD (μm) and GSD (dimensionless) for UD and AD solids were computed from a linear regression of the log-normal distribution. The VMD for a PSD is the particle diameter that is equal to or less than 50% of the volume of particles in the sample. The GSD (σ_g) is defined as the ratio of the particle diameter that is equal to or less than 84.1% (d_{84}) of the volume of particles in the sample and the VMD (d_{50}), or the ratio of VMD (d_{50}) and the particle diameter that is equal to or less than 15.9% ($d_{15.9}$) of the volume of particles in the sample, as shown in equation 7 (Wang et al., 2013; Karanasiou et al., 2007; Redwine et al., 2002):

$$\sigma_g = \frac{d_{84.1}}{d_{50}} = \frac{d_{50}}{d_{15.9}} \quad (7)$$

Microsoft Excel was used for PSD analysis, plotting of graphs, and regressions analyses. The means of mass transfer coefficients and fraction of ammonia in TAN were analyzed using a two-way ANOVA: factor 1 was manure type (UD and AD), and factor 2 was manure temperature (15°C, 25°C, and 35°C). Analyses of variance (ANOVA) for the treatment means were performed using SAS (SAS, 2006). Pairwise comparisons for treatments means were performed using Tukey's Studentized test (HSD) at a significance level of $\alpha = 0.05$.

RESULTS AND DISCUSSIONS

CHEMICAL PROPERTIES OF MANURES

Characteristics of manure before and after AD are presented in table 2. The results showed significantly ($p < 0.05$) greater values of pH, TAN, IS, and viscosity in AD manure as compared to UD manure. The mineralization of organic matter during the AD process was responsible for higher TAN and IS, whereas increased ammonia nitrogen (alkaline in nature) contributed to the higher pH observed in AD manure. Increased viscosity of the manure has been attributed to the breakdown of solid organic matter during the AD process (Goel et al., 2004). These physical and chemical changes following AD of manure affect ammonia volatilization in different ways. On one hand, increased pH and TAN, for instance, may increase the potential for ammonia volatilization from AD compared to UD manure, while higher viscosity may impede ammonia volatilization.

The concentration of TS in UD manure was approximately 48% more than in AD manure (table 2). The lesser amount of VS in AD manure (0.84%) than in UD manure (2.05%) indicated a higher content of organic matter in UD than in AD manure. The former and latter observations were in agreement with theory and with other studies (Martin, 2004; Sommer and Husted, 1995; Ortenblad, 2000; Van Velsen, 1977). An inverse relationship between ammonia dissociation and TS concentration in liquid manure has been reported in past research (Vaddella et al., 2011; Liang et al., 2002; Zhang, 1992), which suggests that the decrease in TS concentration following AD of dairy manure may exacerbate ammonia volatilization.

PARTICLE SIZE DISTRIBUTION CHARACTERISTICS

PSD analysis was performed to characterize solids in the AD and UD manures. PSD statistics and PSD plots of respective manure solids are presented in table 3 and figure 2, respectively. The model MS2000 Mastersizer, with a range of 0.01 to 2000 μm, was used for the PSD analysis. Figure 2 was scaled from 0.1 to 1000 μm in the x-axis because that was the predominant range of PSD in our analysis. The volume median diameters (VMD) of the AD and UD manure solids were not significantly different ($p = 0.65$). However, the respective geometric standard deviations (σ_g) were significantly different ($p = 0.001$) between AD and UD manure solids. These results suggest that UD solid particles were only slightly larger but more widely distributed than the AD manure solids. The PSD of solid particles for the AD and UD manures were heavily right-skewed (fig. 2), indicating higher concentrations of coarse particles.

Table 2. Properties of undigested and anaerobic digested liquid manure. Values are mean ± standard deviations (*n* = 3).

Manure Type	pH	TAN (mg L^{-1})	Viscosity (Pa s)	IS (mol L^{-1})	TS (%)	VS (%)
UD	7.58 ±0.08	480 ±2	0.058 ±0.005	0.228 ±0.001	3.27 ±0.07	2.05 ±0.10
AD	8.20 ±0.05	512 ±3	0.119 ±0.002	0.274 ±0.002	1.71 ±0.10	0.84 ±0.05

Table 3. Particle size statistics for anaerobically digested and undigested manure.[a]

Manure Type	VMD (μm)	GSD (dimensionless)
AD	45.15 a	7.18 a
UD	46.76 a	9.18 b

[a] VMD = volume median diameter; GSD = geometric standard deviation. Means in the same column followed by the same letter are not significantly different at $\alpha = 0.05$.

Table 4. Overall mass transfer coefficients (K_{oL}) for undigested (UD) and anaerobically digested (AD) dairy manure.[a]

Temperature (°C)	K_{oL} ($\times 10^{-6}$ m s^{-1}) UD Manure	AD Manure
15	2.96 aA	1.98 aB
25	2.40 bA	2.13 aA
35	2.06 cA	1.38 bB

[a] Means followed by the same lowercase letter in the same column or by the same uppercase letter in the same row are not significantly different at $\alpha = 0.05$.

In general, organic matter is degraded during the AD process, which may explain the slightly lesser VMD and narrower distribution of solids from AD manure compared to UD manure solids. The PSD of manure solids is an indicator of their relative potential to adsorb TAN. Fine particles, in general, have a higher potential for TAN adsorption than coarse particles. The adsorption of TAN on manure solids effectively reduces ammonia volatilization. The manure solids particle size and PSD analyses, before and after the AD process, did not indicate a large enough change in the TAN adsorption potential of manure solids for this phenomenon to play a significant role in the ammonia volatilization process.

Overall Mass Transfer

The overall mass transfer coefficients (K_{oL}), determined at the three liquid temperatures, as well as the relationships between K_{oL} and liquid temperature, are presented in table 4 and figure 3 for both UD and AD dairy manures. A two-way analysis of variance (ANOVA) showed significantly ($p < 0.001$) greater K_{oL} for the UD manure than for the AD manure (table 4), indicating higher potential for ammonia volatilization from UD compared to AD manure. The ANOVA also indicated significant differences ($p < 0.001$) in the K_{oL} at different temperatures. The K_{oL} for both AD and UD manures decreased with temperature (R^2 = 0.57 and 0.98, respectively). In contrast, previous research reported increases in K_{oL} with increasing manure temperature (Vaddella et al., 2013; Montes et al., 2009; Arogo et al., 2003). For given environmental conditions and fixed manure temperature, the manure properties that may influence K_{oL} are the viscosity, TS concentration, and $NH_{3(L)}$ concentration of the manure. Compared to the UD manure, higher viscosity of the AD manure implied decreased K_{oL}, while increased $NH_{3(L)}$ concentration and lower TS concentration increased the K_{oL}. Overall, therefore, the net effect of lower TS concentration and higher $NH_{3(L)}$ concentration on K_{oL} was evidently significantly lower than the effect of increased viscosity. However, the results also showed significant interaction between temperature and manure on K_{oL} ($p = 0.002$). Pairwise comparisons of the cell means indicated that the K_{oL} values were significantly different at all three temperatures (15°C, 25°C, and 35°C) for the UD manure. On the other hand, although the K_{oL} values were not significantly different between 15°C and 25°C, both of these K_{oL} values were significantly higher than at 35°C for the AD manure. The rate of change of K_{oL} with temperature was higher in the UD manure than in the AD manure. These results suggested that low temperature had more influence on K_{oL} in both the AD and UD manures and, more specifically, the K_{oL} for the UD manure was more sensitive to temperature than for the AD manure.

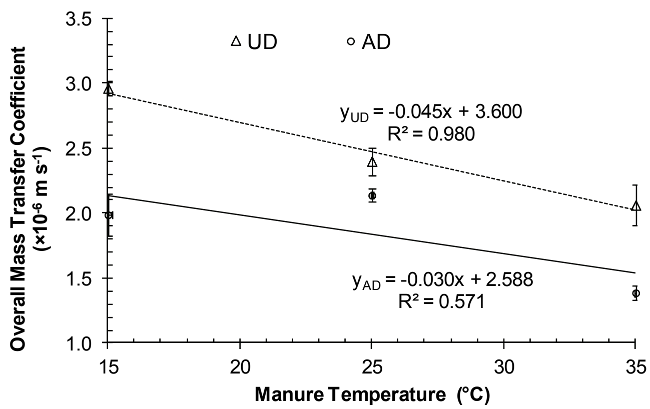

Figure 3. Relationships between the overall mass transfer coefficients (K_{oL}) and temperature for anaerobically digested (AD) and undigested (UD) manures (error bars show standard deviations of means).

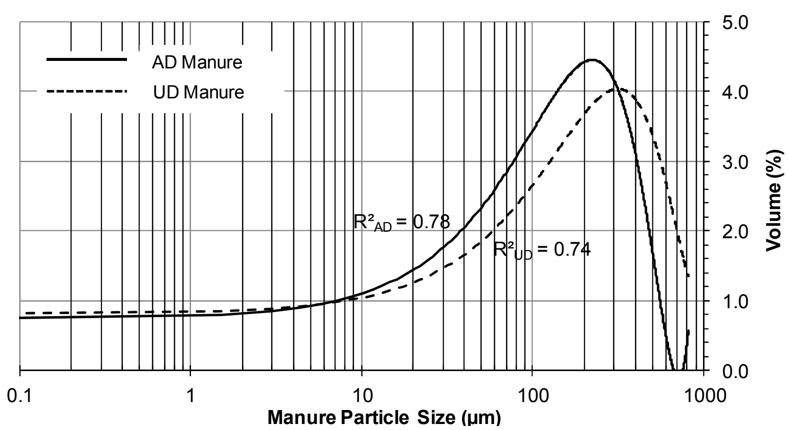

Figure 2. Comparative particle size distribution for anaerobically digested and undigested manures (R^2 = 0.78 and 0.74, respectively).

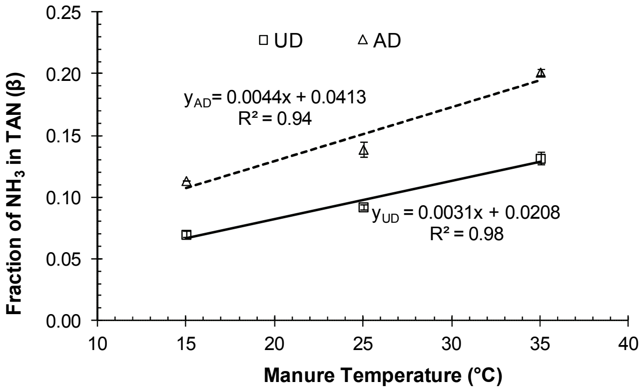

Figure 4. Relationships between fraction of NH_3 in TAN (β) and manure temperature for anaerobically digested (AD) and undigested (UD) manures.

AMMONIUM ION DISSOCIATION

The fraction of NH_3 in TAN (β) is a direct measure of NH_4^+ dissociation in solution or in liquid manure. The values of β used in most ammonia volatilization models are estimated from ammonium dissociation in pure water and incorporate the effects of the ions and solids present in the manure (Montes et al., 2009). Past studies indicated that increases in temperature and pH of the liquid manure increase the ammonium dissociation and thus β (Vaddella et al., 2011; Arogo et al., 2003). The fraction of NH_3 of TAN (β) as a function of temperature and manure type (AD and UD) are shown in figure 4, while ANOVA results are presented in table 5. The proportion of NH_3 in TAN increased with temperature for both manure types, UD and AD (R^2 = 0.98 and 0.94, respectively). The proportion of NH_3 in TAN was not only significantly greater ($p < 0.001$) in AD than in UD liquid dairy manure but also increased significantly ($p < 0.001$) with temperature. The larger β is, the greater the potential of ammonia volatilization from the manure; therefore, these results suggest increased ammonia emission from AD compared to UD liquid dairy manure, which is also exacerbated by increasing temperatures. The observed larger β values for AD manure suggested that the decrease in β as a result of increased IS after AD was more than counteracted by the increase in β resulting from increases in the higher pH and the lower TS concentration of digested manure (table 2). TAN is the sum of ionized NH_4^+ and un-ionized $NH_{3(L)}$; the proportion of each depends on the pH and temperature of the manure solution. Specifically, the NH_3 fraction of TAN (β) in solution increases with the pH of the liquid manure. A two-way ANOVA indicated significant interaction between temperature and manure type on β ($p = 0.005$), which is also evident in figure 4. The linear regressions presented in figure 4 suggest that β was more sensitive to temperature in the AD manure than in the UD manure.

Table 5. Fraction of NH_3 (β) with respect to total ammoniacal nitrogen for undigested (UD) and anaerobically digested (AD) manure.[a]

Temperature	β	
(°C)	UD Manure	AD Manure
15	0.070 aA	0.113 aB
25	0.092 bA	0.140 bB
35	0.132 cA	0.201 cB

[a] Means followed by the same lower case letter in the same column or by the same uppercase letter in the same row were not significantly different at α = 0.05.

Table 6. Changes in manure parameters after anaerobic digestion of dairy manure at manure temperature of 15°C.

Manure Type	Manure Parameter			
	K_{oL} (m s^{-1})	β	TAN (mg L^{-1})	$Q_{Initial}$ (g m^{-2} s^{-1})
UD	2.98 ±0.01	0.070 ±0.002	480 ±2	99.33 ±0.39
AD	1.99 ±0.01	0.113 ±0.000	512 ±3	115.69 ±0.64
AD:UD ratio	0.667	1.614	1.067	1.164

RELATIVE CONTRIBUTIONS OF PARAMETERS

The respective relative net contributions of each parameter to the ammonia volatilization process, at a manure temperature of 15°C, are summarized in table 6. The relative contributions were computed as the ratio of the respective value for the AD manure to that of the UD manure at similar conditions. These results indicate that the largest change in the process was attributable to the increase in the proportion of un-ionized NH_3 of TAN (β) that occurred with AD, which would potentially increase ammonia volatilization by approximately 61%. As discussed earlier, the significant increase in pH from 7.6 to 8.2 was probably predominantly responsible for the higher dissociation of NH_4^+ to $NH_{3(L)}$. Increases were observed in concentration of TAN after AD of manure, which in general also implied increased potential for ammonia volatilization. The contribution of the increases in TAN concentration to the potential increase in ammonia volatilization was approximately 7%. The AD of manure resulted in a 33% decrease in the overall mass transfer of ammonia (K_{oL}). The decrease in K_{oL} was attributed to the increased viscosity after AD of manure. The effective relative increase in initial ammonia flux (i.e., flux at the beginning of storage) from the AD manure compared to the UD manure from the observed changes in K_{oL}, β, and TAN was ~16% at 15°C, according to the ammonia flux model (eq. 4).

CONCLUSIONS

Pertinent physical and chemical characteristics of UD and AD manure that may influence ammonia volatilization process, including PSD, TS, VS, viscosity, pH, TAN, and IS, were determined. The pH, TAN concentration, viscosity, and IS were greater in AD manure than in UD manure. Concentrations of TS and VS were 48% and 59% greater, respectively, in UD manure than in AD manure. Overall, the characteristics of the AD and UD manures that are key to the ammonia volatilization process were significantly different. The GSD values were significantly greater for the UD than AD solids, but the VMD values were not significantly different, indicating that PSD did not significantly alter the ammonia volatilization process. The NH_3 fraction of TAN (β) was significantly greater for AD than for UD. However, the mass transfer coefficient (K_{oL}) was less for AD than for UD manure. The K_{oL} decreased with increase in temperature. On one hand, the net effect of higher pH and lower TS concentration on β following AD was significantly greater than the counterbalancing effect of increased IS. On the other hand, the effect of increased viscosity on K_{oL} following AD was more than counteracted by the effects of lower TS concentration, increased β, and higher TAN concentration. At manure temperature of 15°C, potential increases in the initial ammonia volatilization of approximately 7% and 61% were observed from increases in TAN concentration and β, respectively, with AD of dairy manure. Overall, AD of dairy manure increased the initial ammonia flux by ~16%. Additional strategies may thus be required to mitigate NH_3 emissions following AD of dairy manure.

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