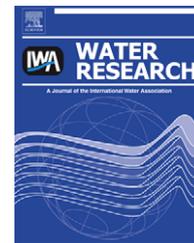


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Modeling of ammonia speciation in anaerobic digesters

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ABSTRACT

Anaerobic digestion of high-nitrogen wastes such as animal manure can be inhibited by high concentrations of un-ionized ammonia, NH_3 (aq). Understanding the toxicity of NH_3 (aq) to anaerobic digestion requires a method for determining its concentration. Previous work on ammonia toxicity in anaerobic digesters has utilized a simple equilibrium calculation for estimating NH_3 (aq) concentration from total ammonia, temperature, and pH. This approach is not appropriate for concentrated solutions. In this work, a speciation model for major solutes in anaerobic digesters, based on Pitzer's ion-interaction approach, is presented. Model simulations show that the simple equilibrium calculation (without corrections for non-ideal behavior) substantially overestimates NH_3 (aq) concentration for all but dilute digesters. This error in concentration determination increases with total solids content and is estimated to be greater than 40% for a digester fed dairy manure with 5% total solids or swine manure with 3% total solids. However, including an estimate of the activity coefficient for NH_4^+ in the simple equilibrium calculation results in much more accurate estimates of NH_3 (aq) concentration. In this case, the estimated error is less than 10% in the absence of struvite precipitation at the highest total solids contents considered.

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1. Introduction

Ammonia toxicity can be a problem for anaerobic digestion of high-nitrogen wastes, such as animal manure. High concentrations of ammonia can reduce biogas quality (i.e., CH_4 content) and production rates (McCarty and McKinney, 1961; De Baere et al., 1984; Zeeman et al., 1985; Hansen et al., 1998). Since un-ionized ammonia, NH_3 (aq), is thought to be the species responsible for ammonia toxicity (McCarty and McKinney, 1961; De Baere et al., 1984) understanding and controlling ammonia toxicity requires an understanding of the mechanisms that control the chemical activity of NH_3 (aq). In anaerobic digesters NH_3 (aq) exists in equilibrium with other forms of nitrogen, including ammonium (NH_4^+), carbamate (NH_2COO^-), and the mineral struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$).

In this paper, the term “total ammonia” is used to refer to the sum of all these chemical species.

Previous work on ammonia toxicity in anaerobic digesters has used a simple chemical equilibrium calculation to estimate NH_3 (aq) concentration using total ammonia, temperature, and pH, as shown in Eq. (1), where c_{NH_3} = NH_3 (aq) concentration (mol/L), $c_{\text{total ammonia}}$ = total ammonia concentration (mol/L), K_a = temperature-specific acid dissociation constant, and pH = measured pH.

$$c_{\text{NH}_3} = \frac{K_a c_{\text{total ammonia}}}{K_a + 10^{-\text{pH}}} \quad (1)$$

This approach is based on the assumptions that solute behavior is ideal and that NH_4^+ is the only species in equilibrium with NH_3 (aq). Neither assumption is accurate for

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concentrated solutions of ammonia and inorganic carbon. A more accurate approach for simulating ammonia speciation would be useful for predicting and controlling ammonia toxicity. Moreover, a comprehensive speciation model for the major solutes in digesters would be useful for other tasks as well, such as predicting biogas composition. In this work a comprehensive speciation model for the major solutes in anaerobic digesters is presented. This model was used to estimate the error in the commonly-used simple equilibrium calculation and to explore speciation of major solutes in manure digesters.

2. Solutes and solute concentrations in manure digesters

The majority of research on ammonia toxicity in anaerobic digestion has focused on cattle and swine manure and these wastes are the focus of this work. At high solute concentrations, it is not possible to consider ammonia speciation in isolation from other chemical systems that exist in manure digesters. Chemical characteristics for several laboratory and full-scale cattle and swine manure digesters are given in Table 1. Comprehensive data on major solutes in manure digesters are not widely available, although data on element concentrations in fresh manure are available (Table 2). Based on these data, the elements N, K, Ca, Cl, P, Mg, Na, and S typically constitute >99% of the total concentration of elements in manure, excluding C, H, and O. Since these elements dominate the composition of the manure only they will be considered further. Inorganic carbon is present at high concentrations in anaerobic digesters, but concentrations in solution are dependent on both the fraction of total manure carbon released as CO₂ via microbial metabolism and the

fraction of this inorganic carbon that remains in solution. Inorganic carbon is explored in more detail below.

3. Description of the speciation model

3.1. Overview

The comprehensive speciation model presented in this work uses Pitzer's ion-interaction approach (Pitzer, 1991) to calculate activity coefficients for aqueous species. This approach is suitable for concentrated solutions where the extended Debye-Hückel or similar approaches are generally not accurate, e.g. ionic strengths greater than 0.1 mol/kg (Pitzer, 1991). Eq. (2) shows the general form of the equation used for calculating activity coefficients in the Pitzer approach.

$$\ln \gamma_M = z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \sum_c m_c \sum_a m_a \psi_{Mca} + \sum_{a<c} \sum_{a'} m_a m_{a'} \psi_{aa'M} + |z_M| \sum_c \sum_a m_c m_a C_{ca} + 2 \sum_n m_n \lambda_{Mn} + 3 \sum_n m_n^2 \mu_{Mnn} + 6 \sum_{n<c} \sum_{n'} m_n m_{n'} \mu_{Mnn'} \quad (2)$$

In Eq. (2), the subscript M indicates the cation of interest, c other cations, a anions, and n neutral species. Additionally, m = solute molality (mol/kg), and z = ion charge. The terms F, B, Z, and C are calculated from functions that are described in Pitzer (1991). The terms B and C incorporate the interaction parameters $B_{c,a}^{(0)}$, $B_{c,a}^{(1)}$, $B_{c,a}^{(2)}$ and $C_{c,a}^{(0)}$. These parameters quantify the effects of interactions between individual cations and anions, while the parameters ψ and μ are for interactions between three species. The parameter λ describes interactions between neutral solutes and other species. Eq. (2) is for cations; equations for anions and neutral species are similar.

Table 1 – Characteristics of laboratory and full-scale digesters treating cattle and swine manure.

Type	T (°C)	Feed solids (%)	Total N	Total ammonia	Total P	Orthophosphate	pH	CH ₄ (%)	CO ₂ (%)	Reference
C	38	11% TS	380	190	28	18	7.92	58	36	Wright et al. (2004)
C	38	8.3% TS	250	160	17	10	7.63	64	30	Wright et al. (2004)
C	38	9.0% TS	300	160	15	10	7.74	58	36	Wright et al. (2004)
C	35	9.7% TS		230			7.72	46–60	34–48	Hafner (2007)
C	50	5.0% TS	140	85			7.68			El-Mashad et al. (2004)
C	55	5.8% VS		240			8.1			Hansen et al. (1999)
C	55	4.2% VS		180			8.0–8.2	51–55	(30–34)	Angelidaki and Ahring (1994)
C	55	9.7% TS		240			7.58	24–57	28–61	Hafner (2007)
S	35	5.2% TS	110	71			7.0–7.3			Boopathy (1998)
S	37	2–5% TS		210			7–8			Braun et al. (1981)
S	37	4.5% VS		420			8.06	67	(27)	Hansen et al. (1999)
S	35	3.0% TS	160	120			6.5–7.4	60	33	Zhang et al. (1990)
S	35	1.9% TS	64	36			7.41	61	(33)	Hill and Bolte (1986)
S	55	4.5% VS		310			8.1			Hansen et al. (1998)
S	55	4.5% VS		430			7.97	43	(42)	Hansen et al. (1999)
S	55	1.2% TS	63	45			7.63	58	(27)	Bolte et al. (1986)

Notes: For Type, C = cattle, S = swine. All concentrations are expressed using the molar scale, as mmol/L, unless otherwise specified. Concentrations of CO₂ and CH₄ are wet volume-based biogas or headspace concentrations, reduced from reported values to correct for water vapor, using values given in ASME (2000). Therefore, these values can be multiplied by the total headspace pressure to estimate partial pressures. Carbon dioxide values given in parentheses are estimated from CH₄ concentrations, assuming all other gases except water vapor are negligible.

Table 2 – Mean dry elemental concentrations in cattle and swine manure, calculated from ASAE (1998) or ASAE (2005).

Dry concentration (% of TS)									
	N	K	Ca	Cl	P	Mg	Na	S	
C	5.1 ^a	1.2 ^a	1.3	1.1	0.88 ^a	0.59	0.43	0.43	
S	8.4 ^a	3.6 ^a	3.0	2.4	1.4 ^a	0.64	0.61	0.69	
	Fe	B	Mn	Zn	Cu	Ni	Mo	Cd	Pb
C	0.10	0.0059	0.016	0.015	0.0038	0.0023	0.0006	0.00003	NA
S	0.15	0.028	0.017	0.045	0.011	NA	0.0003	0.0002	0.0008

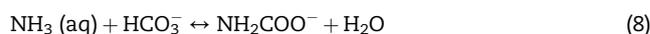
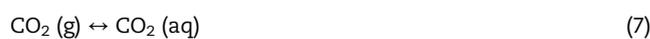
Notes: C = dairy cattle and S = swine. Values with an “a” superscript are from ASAE (2005), all others are from ASAE (1998). NA = not available.

More details can be found in Pitzer (1991), Clegg and Whitfield (1991), and Plummer et al. (1988).

This speciation model was implemented using the USGS chemical speciation program PHREEQC (version 2.15.0-2697) (Parkhurst and Appelo 1999) (available from http://wwwbr.cr.usgs.gov/projects/GWC_coupled). With PHREEQC, species, reactions, equilibrium constants, and Pitzer interaction parameters are all defined in a “database” file. For implementing the model described in this work, a new database file that contains data for the reactions described below was developed. This new database file is described in the following sections and can be found online in the [Supplementary data](#).

3.2. Species, reactions, and model parameters

Simple speciation calculations using the data in Table 1, available measurements (Hafner and Bisogni, 2007), and approximations based on charge balance all indicate that the inorganic carbon species HCO_3^- and CO_3^{2-} collectively contribute the majority of anion concentration in manure digesters. Given a solution with high concentrations of total NH_3 and inorganic C, previous work has shown that the following species must be considered for successful speciation modeling: NH_4^+ , NH_3 , CO_3^{2-} , HCO_3^- , CO_2 , and NH_2COO^- (Edwards et al., 1978; Kamps et al., 2000). Relevant reactions for these species are shown below as Reactions (3)–(8).

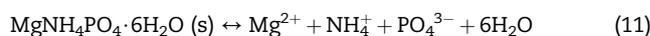


The response of equilibrium constants to temperature can be described in PHREEQC using Eq. (10).

$$\log K = A_1 + A_2T + \frac{A_3}{T} + A_4 \log T + \frac{A_5}{T^2} \quad (10)$$

where K = equilibrium constant, T = temperature in K, and A_1 through A_5 are empirical constants. Coefficients for the calculation of equilibrium constants for Reactions (3)–(9) (i.e., A_1 through A_5 in Eq. (10)) were taken directly or calculated from Kamps et al. (2000). Resulting coefficients are given in Table 3 for Reactions (3)–(9).

The mineral struvite has been shown to precipitate in both swine and dairy manure (Burns and Moody, 2002; Gungor et al., 2007) and, therefore, it was included in the database via Reaction (11). Coefficients for the solubility constant (i.e., A_1 through A_5 in Eq. (10)) were calculated from the solubility constants given in Aage et al. (1997).



The new database file also includes: the orthophosphate and the sulfide systems; complexes between inorganic C and orthophosphate anions and Ca, Mg, Na, and K cations;

Table 3 – Coefficients used to calculate thermodynamic equilibrium constants as a function of temperature, via Eq. (10).

Reaction	A_1	A_2	A_3	A_4	A_5
3	18.656	0.0048326	–3263.8	–7.4138	
4	–2.7019		816.05		154,233
5	–50.696	0.0096626	3900.8	18.112	
6	–44.420	0.012206	3362.6	14.506	
7	–84.759	–0.0062570	4179.8	28.749	
8	8.6063	0.0020367	240.03	–4.0400	
9	61.206		–5839.5	–22.477	
11	–292,902	–53.478	13,949,154	109,013	–684,213,274

Notes: Coefficients were recalculated from Kamps et al. (2000) for all reactions except (11), which were calculated from data given in Aage et al. (1997). For gas dissolution (i.e. Henry’s constants) the standard pressure is 1 atm.

equilibrium between liquid water and water vapor, and methane equilibrium between solution and gas. Coefficients for calculating equilibrium constants for these species were taken from Rumpf and Maurer (1994), the Pitzer database file distributed with PHREEQC (Pitzer.dat, the derivation of which is described in Plummer et al. (1988)), or the NIST stability constant database (Martell and Smith, 2004) as listed in the new database file. The solubility of methane was fixed at 0.001 mol/kg-atm based on Duan et al. (1992).

3.3. Pitzer interaction parameters

Pitzer parameters for interactions among all ammonia and inorganic C species were taken from Kamps et al. (2000). Where coefficients for the response of parameters to temperature were provided, coefficients were transformed into the format used by PHREEQC. In cases where direct transformation was not possible, coefficients were estimated from least-squares regression of parameter values predicted using the equations given in Kamps et al. (2000) at 1 K increments. Coefficients are given in the Supplementary data. Parameters for relevant interactions present in the database file Pitzer.dat were used directly.

3.4. Model simulations

The model simulations presented here represent chemical equilibrium within a two- or three-phase system containing digested manure, an associated gaseous phase (i.e. biogas), and in some cases, the mineral struvite. Since CH₄ and CO₂ concentrations represent total biogas production, simulations represent a batch digester at the end of a cycle or a continuously-fed digester at steady-state. Solute concentrations were specified as model input based on the feed total solids (TS) concentration and element concentrations in manure on a TS basis. This approach assumes that water losses and gains during digestion are negligible relative to the water introduced in the influent. This assumption can be shown to be reasonable based on expected evaporative and metabolic water loss (Richards et al., 1991). In these simulations, all particulate matter is assumed to be inert with regard to chemical speciation. All model simulations assume equilibrium.

To explore speciation of ammonia and inorganic C in digesters, predictions were made for dairy and swine manure at feed TS concentrations of 0.1–15% and 0.1–10%, respectively, at 35 °C and 55 °C. Concentrations of all solutes were taken from the data shown in Table 2, with the exception of

CO₂ and CH₄. The concentrations of CO₂ and CH₄ were estimated from ASAE (2005) by assuming that manure volatile solids are 50% C by mass, and that 20% of this C is converted to CO₂, and 20% is converted to CH₄. This approximation is based on measurements given in Hafner (2007) as described in the Supplementary data. Sixty percent of N and P were assumed to be present as total ammonia and orthophosphate, respectively (Table 1, Ajiboye et al., 2004). All other elements were assumed to be present only as inorganic species. Charge balance was attained in all simulations by simulating the addition of all solutes as acids or bases (Table 4). Solution pH was not specified but was predicted, except when the model was used to calculate NH₃ (aq) in specific digesters (i.e. Tables 6 and 7).

Precipitation of minerals in anaerobic digesters affects speciation. Mineral precipitation removes solutes from solution, which can directly and indirectly influence speciation, including pH. However, mineral phases such as struvite may not reach equilibrium in anaerobic digesters because of kinetic limitations or sorption of cations to organic matter. In this work, both extremes were simulated for the mineral struvite only: no mineral precipitation, and precipitation to equilibrium.

The model developed by Kamps et al. (2000), from which the model parameters for the most important reactions and interactions come for this work, does not include interactions between ions of like charge, but does include the parameter μ for interactions between two neutral species and a third species (Supplementary data). These options are now available in PHREEQC starting with version 2.14.3 (D. Parkhurst, pers. comm.). For all the simulation results presented in this work, the parameter $\epsilon\theta_{i,j}(I)$ was set to zero (Plummer et al., 1988).

The simple equilibrium calculation can be improved by incorporating the activity coefficient of NH₄⁺, as given in Eq. (12).

$$m_{\text{NH}_3} = \frac{K_a \gamma_{\text{NH}_4^+} m_{\text{total ammonia}}}{10^{-\text{pH}} + \gamma_{\text{NH}_4^+} K_a} \quad (12)$$

Eq. (12) was derived from mass balance and mass action expressions, and is based on the assumptions that $\gamma_{\text{NH}_3(\text{aq})}$ is unity, NH₄⁺ and NH₃ (aq) are the only ammonia species present, and that 10^{-pH} is equal to the activity of H⁺. To test this approach, $\gamma_{\text{NH}_4^+}$ was calculated using the extended Debye-Hückel equation (Stumm and Morgan, 1996) with A and B parameters calculated based on the equations given in Pitzer (1991) and the ion size parameter taken from Kielland (1937) (set to 2.5). Error in Eqs. (1) and (12) was estimated for all the conditions described above by taking results from the comprehensive model as “true” values.

Table 4 – Solute concentration data used in model simulations. Concentrations were calculated from the values given in Table 2, assuming 60% of total N and total P are present as ammonia and orthophosphate, respectively (Table 1, Ajiboye et al., 2004).

CO ₂	CH ₄	NH ₃	KOH	Ca(OH) ₂	HCl	H ₃ PO ₄	Mg(OH) ₂	NaOH	H ₂ S
<i>Dairy manure concentrations (mol/kg)</i>									
7.02	7.02	2.17	0.296	0.333	0.306	0.170	0.243	0.188	0.133
<i>Swine manure concentrations (mol/kg)</i>									
6.69	6.69	3.60	0.913	0.749	0.667	0.263	0.262	0.265	0.215

Notes: All values are on a dry matter basis, i.e. quantity of solute per unit mass total solids. See the Supplementary data for details on CO₂ and CH₄.

4. Results

4.1. Predicted speciation of total ammonia and inorganic carbon

For all conditions, the cation and anion with the highest concentrations are NH_4^+ and HCO_3^- (results for dairy manure at 35 °C are shown in Fig. 1, other conditions, which show similar trends, can be found in Supplementary data). Due to an increase in pH as TS concentration increases, the relative concentrations of NH_3 (aq) and NH_2COO^- both increase. Solution pH is predicted to increase with TS concentration, but after an initial decline in CH_4 partial pressure and corresponding increase in CO_2 partial pressure, gas composition is relatively stable. Predicted biogas composition is similar to values from Table 1. The activity coefficient of NH_4^+ is predicted to significantly decrease as TS concentrations increase, resulting in substantial error in the simple equilibrium calculation (Eq. (1)), as discussed below. Conversely, $\gamma_{\text{NH}_3(\text{aq})}$ is predicted to be within 0.02 of unity for all simulations. Allowing struvite to form slightly reduces the concentration of nitrogen species and pH for all scenarios (Supplementary data). Struvite contains a maximum of 7.7% of the total ammonia for dairy manure at 35 °C and 15% TS.

4.2. Predicted error in the simple equilibrium calculation

Application of the simple equilibrium calculation given in Eq. (1) results in substantial errors for all scenarios, with swine

manure showing the greatest error: approximately 75% at 10% TS and 35 °C without struvite (Fig. 2). For simulations with struvite, error in Eq. (1) is higher than without, and reaches a maximum in these simulations of 87% at 10% TS and 35 °C for swine manure. With or without struvite precipitation, error in the simple equilibrium calculation (Eq. (1)) is strongly related to $\gamma_{\text{NH}_4^+}$, although other factors play a role as well. This suggests that Eq. (12) may provide reasonable estimates of NH_3 (aq) concentration. The extended Debye–Hückel equation slightly overestimates the activity coefficient of NH_4^+ , but calculated values of $\gamma_{\text{NH}_4^+}$ are close to values predicted by the comprehensive model (Fig. 3). In the absence of struvite precipitation, Eq. (12) predicts very similar results to the comprehensive model, with an error of less than 5% for most cases, and less than 10% at higher TS concentrations (Fig. 4). With struvite precipitation allowed, the error reaches 17% for swine manure at 55 °C and 10% TS. In all cases, the error is much lower than for Eq. (1). Application of this approach requires an estimate of ionic strength. Least-squares regression was used to develop equations for predicting ionic strength from feed TS; resulting coefficients are given in Table 5. These equations were developed from manure with the composition given in Table 4. Application to manure with different solute concentrations, pH, or biogas composition will contribute some error to the results. If possible, measured solute concentrations should be used to estimate ionic strength.

Application of the simple equilibrium calculation and the comprehensive model to four digesters shown in Table 1 is shown in Table 6. Estimated error in the simple equilibrium

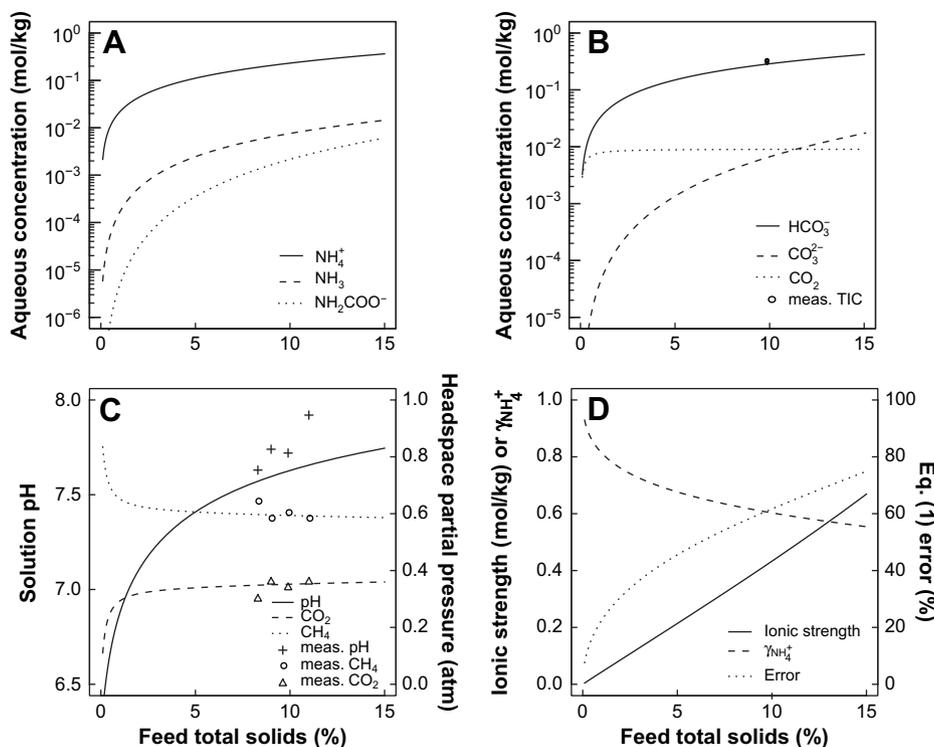


Fig. 1 – Model predictions for dairy manure at 35 °C without struvite precipitation. Panels (A) and (B) show speciation of total ammonia and inorganic C, respectively. Panel (C) shows biogas composition and solution pH. In panel (C), points represent measured values from Table 1. Panel (D) shows ionic strength, $\gamma_{\text{NH}_4^+}$, and the error in Eq. (1).

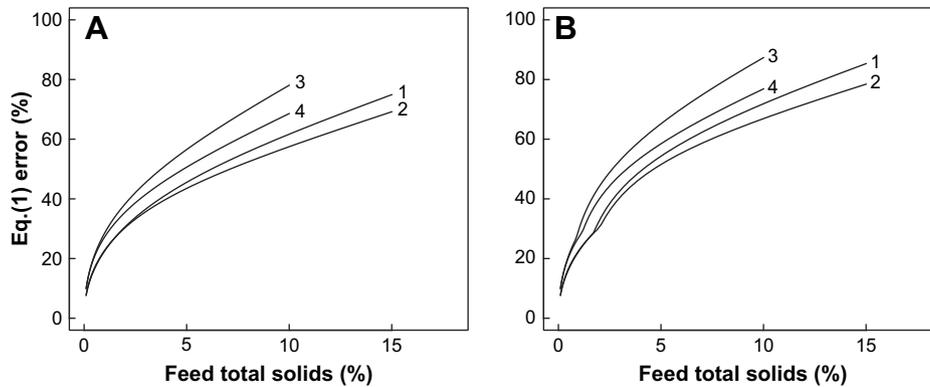


Fig. 2 – Error in the simple equilibrium calculation (Eq. (1)) as compared to predictions from the comprehensive speciation model vs. feed total solids for simulations without (A) and with struvite (B). Lines show dairy manure at 35 °C (1), dairy manure at 55 °C (2), swine manure at 35 °C (3), and swine manure at 55 °C (4).

calculation ranges from 36% to 75% for these digesters. These results provide estimates of the error in the simple equilibrium calculation that can be expected for digesters with characteristics similar to those in Table 6.

Without better information on solute concentrations in anaerobic digesters it is difficult to determine the effect of expected differences in solute concentrations on simulated speciation and errors in Eqs. (1) and (12). The magnitude of error in the simple equilibrium calculation is largely a function of ionic strength and therefore is not very sensitive to changes in the relative solute concentrations. However, the composition of a solution does influence species activities and therefore the error in the Debye–Hückel equation or similar approaches. The assumptions described above for determining concentrations of total ammonia and orthophosphate and production of CO₂ and CH₄ have some effect on these results. For example, assuming that total ammonia is 100% of the nitrogen in manure (as opposed to 60% for the results shown above) results in higher ionic strength at a given TS content and greater error in Eq. (12) (above 15% for swine manure without struvite and above 20% for swine manure with struvite at the highest TS content tested). Reducing CO₂ production to 10% of volatile solids carbon (as opposed to 20% for the results shown above) results in higher solution pH values, and a smaller increase in the error in Eq. (12). Conversely, eliminating all orthophosphate from the simulations only slightly changes results (apart from eliminating struvite).

4.3. Example applications

Two example applications of the comprehensive speciation model are presented. The first example demonstrates the effect of CO₂ volatilization and resulting pH change on the gradient that controls NH₃ volatilization. This process is expected to be important when digested manure is exposed to the atmosphere, e.g., following land application. However, the mass of manure that approaches equilibrium may be small and close to the exposed manure surface. For this simulation, anaerobically digested dairy manure in equilibrium with a gas phase with a total pressure of 1.0 atm was simulated using the

concentrations given in Table 4 at a TS content of 8% (i.e. Table 4 values $\times 0.08696$ kg/kg). Predicted partial pressures show that CO₂ equilibration with the atmosphere (approximately 3.8×10^{-4} atm) increases the equilibrium partial pressure of NH₃ (g) by more than one order of magnitude (Fig. 5).

The second example concerns the variation in biogas quality resulting from different concentrations of total ammonia. In this case, NH₃ concentration was varied from approximately 0.09 mol/kg to 0.28 mol/kg, representing the typical value given in Table 4 $\pm 50\%$ at 8% TS. All other solutes were held at the concentration calculated from the data in Table 4 at 8% TS. In each case, the solution was simulated to be in equilibrium with a headspace with a total pressure of 1.0 atm. Results show an increase in headspace CH₄ partial pressure, from approximately 0.55 to 0.65 atm (58–69% as dry concentrations) as total NH₃ increases. This response is due to increased concentrations of inorganic carbon in solution and

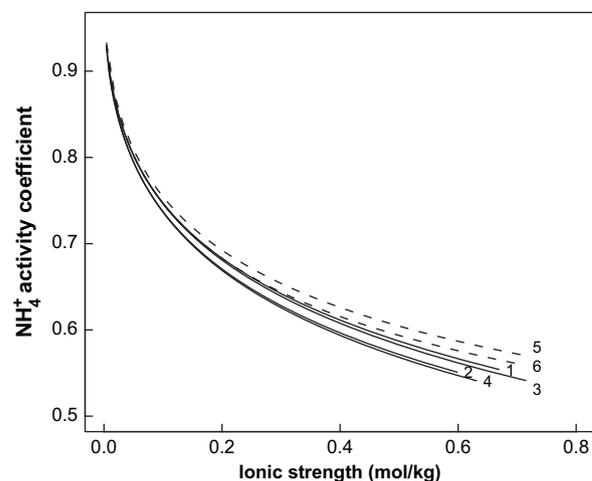


Fig. 3 – Calculated values of $\gamma_{\text{NH}_4^+}$ from the comprehensive speciation model for dairy manure at 35 °C (1), dairy manure at 55 °C (2), swine manure at 35 °C (3), and swine manure at 55 °C (4). The dashed lines show predictions from the extended Debye–Hückel approach for 35 °C (5) and 55 °C (6).

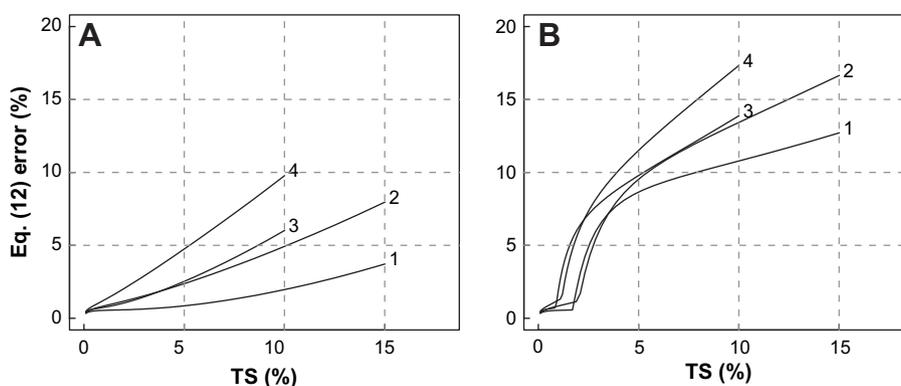


Fig. 4 – Error in Eq. (12) relative to predictions from the comprehensive speciation model vs. feed total solids for simulations without (A) and with struvite (B). Lines show dairy manure at 35 °C (1), dairy manure at 55 °C (2), swine manure at 35 °C (3), and swine manure at 55 °C (4).

is an example of the effect that manure chemistry can have on biogas quality even in the absence of any differences in microbial metabolism.

4.4. Evaluation of model performance

Few measurements of NH_3 (aq) concentration or activity in anaerobic digesters are available (Hafner et al., 2006). We compared predicted and measured NH_3 (aq) concentration for three samples from an intermittently fed mesophilic manure digester. For more details on the digester and the measurement technique, see Hafner et al. (2006) and Hafner (2007). Total ammonia, pH, and temperature were measured for each sample as described in Hafner et al. (2006). For all simulations, the concentration of inorganic C was taken as the mean of measurements made on five occasions (0.33 mol/kg) using the method described by Hafner and Bisogni (2007). Concentrations of other elements were estimated from the data in Table 4 given a TS concentration in the feed of 12%. Activities were scaled using the MacInnes convention (Plummer et al., 1988), which in these simulations influences the concentration of H^+ , since pH is specified and interpreted as $-\log(a_{\text{H}^+})$. Modeled NH_3 concentrations and activities are close to values measured in the laboratory-scale mesophilic digester, but all are slightly below measured values (Table 7). Use of unscaled activities results in slightly lower modeled concentrations and activities.

5. Discussion

5.1. Model limitations

Sources of error in predictions from the comprehensive model include inaccuracy in the model itself and error due to simplification of the chemical system. Data from Kamps et al. (2000) provide some indication of model error. Kamps et al. (2000) compared model predictions to measured CO_2 (g) and NH_3 (g) partial pressures for systems containing NH_4Cl (4 mol/kg), NH_3 (3.9 mol/kg), and CO_2 (0–3.8 mol/kg) near 40 °C. Model predictions of NH_3 (g) partial pressure were within 6% of measured values if the uncertainty in measured values is included. For CO_2 , model predictions were within 36% of measured values, although in most cases the error was much less. The model presented in this work includes additional species, but solutions contain much lower solute concentrations than those of Kamps et al. (2000). These differences would be expected to lead to larger and smaller errors, respectively.

Simplification of the chemical system by ignoring mineral precipitation, interactions between inorganic and organic components, and disequilibrium between headspace and solution may contribute to errors in model predictions. The potential effect of mineral precipitation was explored above

Table 5 – Regression coefficients for estimating ionic strength in digesting manure from feed total solids content via the following equation: $I = C_1S + C_2S^2 + C_3S^3$, where S = total solids as a percentage of wet mass.

Condition	C_1	C_2	C_3	R^2
Dairy, 35 °C	0.04317	-0.0001624	0.00001717	1.000
Dairy, 55 °C	0.04201	-0.0006608	0.00003488	1.000
Swine, 35 °C	0.07564	-0.001425	0.0001014	1.000
Swine, 55 °C	0.07145	-0.002385	0.0001571	1.000
Dairy, 35 °C, struvite	0.04187	-0.0009273	0.00004463	0.9999
Dairy, 55 °C, struvite	0.04172	-0.001527	0.00006554	0.9999
Swine, 35 °C, struvite	0.07338	-0.002862	0.0001726	0.9999
Swine, 55 °C, struvite	0.07099	-0.004103	0.0002441	0.9999

Note: R^2 is the coefficient of determination.

Table 6 – Calculated NH_3 (aq) concentrations for dairy and swine manure digesters.

Type	TS (%)	Total ammonia concentration	pH	T (°C)	NH_3 (aq) concentration/activity		Ref.	
					Eq. (1)	Pitzer model		
								Conc.
Dairy	11	210	7.92	38	24	15	15	1
Dairy	5.0	190	8.1	55	67	49	49	2
Swine	5.6	450	8.06	37	63	36	36	3
Swine	5.6	450	7.97	55	132	79	80	3

Notes: Concentrations of all solutes except ammonia and H^+ were calculated from the TS content using the values given in Table 4. Where only VS content was reported, TS was estimated assuming dairy manure TS is 84% VS, and swine 80% (ASAE, 2005). Concentrations of all solutes except NH_3 and inorganic carbon were estimated from TS content, using the values given in Table 4. Inorganic carbon concentration was determined based on charge balance, and ranged from 0.16 to 0.45 mol/kg. Digester data are from: (1) Wright et al. (2004), (2) Angelidaki and Ahring (1994) and (3) Hansen et al. (1999). All concentrations are in mmol/kg, and the standard concentration for activities is 1 mmol/kg. Both activities and concentrations are given for the comprehensive speciation model predictions.

for struvite. However, additional minerals, such as calcium carbonates and calcium phosphates, have the potential to form in digesters. Excluding mineral phases that actually exist in digesters would cause overestimation of species concentrations resulting in overestimation of the effects of species interactions. In general this would lead to a negative error for predicted NH_3 (aq) concentration and activity. With the possibility of multiple minerals that share common ions, equilibrium modeling alone is not sufficient for predicting the phases present and a kinetic model or assumptions about the relative importance of specific minerals is required. Available measurements show that minerals are important at least for P

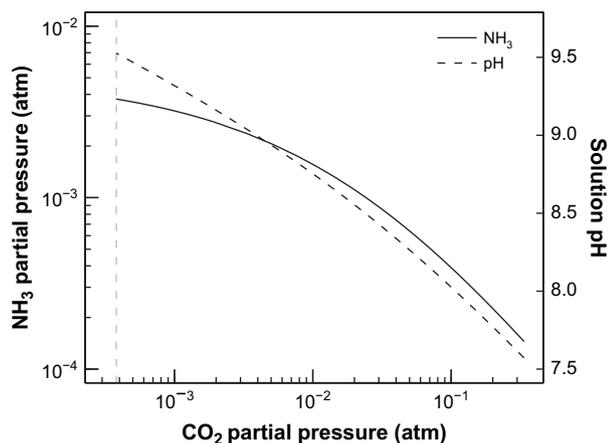


Fig. 5 – Predicted solution pH and NH_3 equilibrium partial pressure in digested dairy manure as a function of CO_2 equilibrium partial pressure. The vertical dashed line represents atmospheric CO_2 partial pressure (3.8×10^{-4} atm).

Table 7 – Measured and modeled NH_3 (aq) concentrations for a laboratory-scale mesophilic digester.

Total ammonia concentration	pH	T (°C)	NH_3 (aq) concentration/activity			
			Measured	Eq. (1)	Pitzer model	
						Conc.
231 (± 10.5)	7.52	35.3	6.1 (± 0.28)	10.4	5.8	5.7
249 (± 19.9)	7.48	35.0	6.0 (± 0.83)	10.0	5.6	5.5
220 (± 8.8)	7.55	35.4	6.6 (± 0.33)	10.7	6.0	5.9

Notes: All concentrations are in mmol/kg, and the standard concentration for activities is 1 mmol/kg. Measured values of NH_3 (aq) represent activities, while Eq. (1) assumes activities and concentrations are equal. Both activities and concentrations are given for the comprehensive speciation model predictions. Values in parentheses represent 95% confidence intervals ($n = 3$ for total ammonia, $n = 10, 5,$ and 10 for the first, second, and third measured NH_3 (aq) values, respectively). See Hafner et al. (2006) for a description of the measurements.

in digested manure. Gungor and Karthikeyan (2008) found that only 7% of the P in digested dairy manure was present in dissolved form. Using X-ray diffraction and X-ray adsorption spectroscopy, Gungor et al. (2007) found that struvite was the dominant form ($\sim 80\%$) of particulate P (25–53 μm size fraction) in digested dairy manure with hydroxylapatite making up the remainder.

Ignoring organic matter interactions has the potential to lead to overestimates of pH. Typical volatile fatty acids (VFA) concentrations, e.g. < 2 g/kg as acetic acid contribute a small amount of charge (< 0.033 mol/kg) compared to the inorganic anion charge but can influence pH (Braun et al., 1981; Angelidaki and Ahring, 1993, 1994). Accurate prediction of pH using this or any other modeling approach will require consideration of the contribution of VFAs, and possibly uncharacterized organic matter. Assuming pH can be accurately measured and is used as a model input (the expected typical application), organic matter only has an effect through interactions with other solutes. Binding of cations to organic matter (Kinniburgh, 1996) would reduce solution concentrations of species and have an effect similar to mineral precipitation. Ammonium might be expected to bind to dissolved or particulate organic matter, but this effect has not been sufficiently studied.

In an actual digester, gas headspace and solution are not in equilibrium unless biogas evolution has ceased. Therefore, the assumption of equilibrium will result in an underestimation of the aqueous concentrations of volatile solutes (i.e. CO_2). Comparison between results found here and values from the literature suggest that this source of error is not large (Fig. 1). Laboratory measurements under a range of conditions could provide some information on this problem. An additional complication in applying these results to full-scale digesters is that pressure, and therefore equilibrium conditions, vary with depth.

Given these limitations in the comprehensive speciation model presented in this work, the model should be taken as a starting point for predicting speciation of major solutes. Although initial comparisons with measured NH_3 (aq) are constructive (Table 7), additional evaluation is necessary.

5.2. Error in the application of the simple equilibrium calculation to anaerobic digesters

Predictions of speciation of total ammonia made using the comprehensive model demonstrate the importance of inorganic solutes in influencing NH_3 (aq) concentration and activity. Results show that estimates of NH_3 (aq) concentrations in anaerobic digesters made using the simple equilibrium calculation (Eq. (1)) are likely to be substantial overestimates. Since this error is dependent on solution composition, it will differ among digesters. For manure with a fixed composition on a TS basis, error will increase with TS content. It is important to note that the simulations presented in this work do not cover the entire range of possible conditions for anaerobic digester chemistry, and the predicted error in Eq. (1) is not dependent on TS alone. However, since typical element concentrations were used in this work, the results can be taken as approximate estimates of the expected error as a function of TS. These results are consistent with direct measurements of NH_3 (aq) activity in anaerobic digesters. Clearly, it is necessary to re-evaluate previous estimates of NH_3 (aq) toxicity thresholds.

5.3. Predicting speciation of total ammonia and other solutes in anaerobic digesters

The comprehensive model described in this study is an appropriate approach for simulating total ammonia speciation in anaerobic digesters. In addition to predicting NH_3 (aq) concentration and activity, this model can be used for simulation of all major solutes in digesters which could be useful for exploring novel digester configurations or predicting the effect of digester manipulations on solution chemistry and biogas composition. Other speciation models have been applied to anaerobic digesters, including both kinetic (Wentzel et al., 2001) and equilibrium (Bril and Salomons, 1990) models. Additionally, free software such as VMINTEQ or PHREEQC can be used to simulate speciation with the extended Debye–Hückel or Davies equations for calculation of activity coefficients. The difference between these models and the comprehensive model presented here is the use of the Pitzer approach for calculating activity coefficients.

Given the similarity between predictions of $\gamma_{\text{NH}_4^+}$ using the extended Debye–Hückel equation and the comprehensive model presented here, as well as the uncertainties inherent in the comprehensive model, a speciation model with activity coefficients calculated using the extended Debye–Hückel or a similar approach may provide sufficient accuracy for many applications. Alternatively, estimates of $\gamma_{\text{NH}_4^+}$ can be used with solution pH, temperature, and total ammonia concentration to estimate NH_3 (aq) concentration using Eq. (12) with some loss of accuracy. Any of these approaches would be expected to be more accurate than the simple equilibrium calculation given in Eq. (1). In any of these cases interpretation of measured pH as $-\log(a_{\text{H}^+})$ is a potential source of error, although the magnitude of this error is probably small (Covington et al., 1985). Additional evaluation of these approaches is needed.

The comprehensive model is suitable for simulating speciation in other types of anaerobic digesters in addition to those treating manure. Other high-nitrogen wastes where ammonia

inhibition may be a problem include the organic fraction of municipal solid waste (El Hadj et al., 2009), meat industry waste (Buendia et al., 2009), and fish processing wastes (Gumisiriza et al., 2009). Previous studies on these materials have applied the simple equilibrium calculation for estimating NH_3 (aq) concentrations. Given the high concentrations of ammonia and other solutes in these materials, the simple equilibrium calculation would be expected to be inaccurate. Application of the comprehensive model is not limited to anaerobic digesters. This model can be applied to manure in general (e.g. Fig. 5) and other materials that contain the same solutes.

6. Conclusions

This paper presents a model for predicting chemical speciation of major solutes in anaerobic digesters using Pitzer's ion-interaction approach. This model can be used to predict NH_3 (aq) concentration and activity in concentrated solutions and has the potential to be useful for modeling digester chemistry and biogas composition. Model predictions show that the simple equilibrium calculation for estimating NH_3 (aq) concentration (without corrections for non-ideal behavior) substantially overestimates NH_3 (aq) concentration for all but very dilute manure digesters. However, incorporation of the activity coefficient of NH_4^+ into this simple approach results in much more accurate estimates and provides an alternative to the more complex comprehensive speciation model presented in this work.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at [doi:10.1016/j.watres.2009.05.044](https://doi.org/10.1016/j.watres.2009.05.044).

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