

Dinitrogen and methane gas production during the anaerobic/anoxic decomposition of animal manure

Lowry A. Harper · Kim H. Weaver ·
Alex De Visscher

Received: 14 February 2014 / Accepted: 10 July 2014 / Published online: 31 July 2014
© The Author(s) 2014. This article is published with open access at Springerlink.com

Abstract Trace-gas emissions from animal feeding operations (AFOs) can contribute to air quality and global change gases. Previous and current estimated gas emissions from AFOs vary widely and many do not consider all forms of carbon (C) and nitrogen (N) emissions. Studies have found that as methanogenesis in the lagoons increased, conversion of ammonium (NH_4^+) to dinitrogen (N_2) also increased. The purpose of this research was to measure N_2 and CH_4 emissions from swine AFOs in three locations of the U.S. and to evaluate the possible universal relationship between lagoon methanogenesis and the conversion of NH_4^+ to N_2 gas. This relationship was tested by measuring N_2 and CH_4 emissions in two climates at 22 different farms. Methanogenesis was correlated with NH_4^+ -to- N_2 conversion by a near-constant N_2 to CH_4 emissions ratio of 0.20, regardless

of C loading and climatic effects. The process is shown to be thermodynamically favored when there is competition between NH_4^+ oxidizing reactions. Under methanogenic conditions (redox potentials of methanogenesis) N_2 production is favorable and nitrification/denitrification is not. Thus, N_2 production is stimulated in methanogenic conditions. Evaluation of NH_3 gas emissions from AFOs must consider other N emissions than NH_3 . Finally, a statistical model was developed to estimate methane and N_2 emissions (kg gas ha^{-1}) given feed input per lagoon surface area (kg feed ha^{-1}) and local air temperature. Further studies are needed to investigate the mechanisms involved in manure processing and isolate the favorable mechanisms into engineering improved manure processing.

Keywords Ammonium · Methane · Methanogenesis · Thermodynamics · Lagoon · Dinitrogen

L. A. Harper (✉)
Lowry A. Harper Consulting Co.,
P.O. Box 772, Watkinsville, GA 30677, USA
e-mail: lowry.harper.pe@gmail.com

K. H. Weaver
Department of Physical Science, Southern Utah
University, 351 W. Center, Cedar City, UT 84720, USA

A. De Visscher
Department of Chemical and Petroleum Engineering, and
Centre for Environmental Engineering Research and
Education (CEERE), University Calgary, Calgary,
AB T2N 1N4, Canada

Introduction

Ammonia (NH_3) is a significant air pollutant, especially in combination with acid gas production from fossil fuel combustion, because the resulting acid–base reaction potentially leads to an air quality problem in the form of haze and respirable particulate matter (PM). The link between PM and increased

mortality is well established (Pope et al. 2002; Cohen et al. 2005). Ammonia emissions' estimates from swine manure treatment lagoons, as a percent of feed nitrogen (N) input, have been reported to vary from 36 to 71 % (Doorn et al. 2002a; Hatfield et al. 1993; USEPA. 2004). From a systems' analysis approach using the *USEPA National Emissions Inventory* (USEPA, 2004), the addition of all NH₃ emissions' components, such as from housing (22 %), lagoons (43 %), field application of manure (23 %), N leaving as animal protein (30 %, from host data), suggest that more than 100 % of the N entering the farm system is leaving the farm as NH₃ volatilization plus animal product. Recent studies in North Carolina (NC) (Harper et al. 2004b), the Georgia Coastal Plains (GA) (Harper and Sharpe 1998; Harper et al. 2000), and the Central Great Basin (CGB) (Harper et al. 2010; Weaver et al. 2012) regions have shown that swine lagoons emit significantly less NH₃ than previously and currently thought. Much of the N estimated as NH₃ gas emissions has been found to be converted to dinitrogen gas (N₂) (Harper et al. 2000, 2004b; Weaver et al. 2012), representing an even larger discrepancy for the N balance of farm systems suggested by the USEPA. This aspect of dinitrogen emissions, not considered in most of the estimates of NH₃ emissions from animal feeding operations (AFOs), highlights the fact that the N cycle in lagoons is not fully understood. Benign N₂ emission from lagoons is a pathway of N emissions is that is significant and must be considered in the total N balance of AFOs. When the National Emissions Inventory (USEPA 2004) NH₃ emissions values are combined with published (measured) N₂ emissions (Harper et al. 2000, 2004a, b; Weaver et al. 2012), in many cases more N as NH₃ plus N₂ is emitted than is excreted by the animals, suggesting the need to reevaluate emissions' estimates.

Many of the current NH₃ emissions' estimates are based upon chamber measurements. A number of studies using dynamic chamber measurements (Aneja et al. 2000; Blunden and Aneja 2008) have led to higher emission estimates than found by micrometeorological measurements (Harper and Sharpe 1998; Harper et al. 2000, 2004b, 2010). Doorn et al. (2002b) pointed out that studies with dynamic chambers led to emission factors 2.3 times higher than studies with micrometeorological techniques, while others (Shah et al. 2006; Rochette et al. 1992; Harper 2005; Harper et al. 2010;

2011) stated that chamber techniques are not even suitable for developing emission factors as they create conditions at the water surface that overestimate NH₃ emissions. Based on all of the evidence (Harper et al. 2000, 2004b; Weaver et al. 2012) and discussions regarding the physical chemistry of highly anaerobic systems (van Cleemput 1972, 1997), it seems very plausible that NH₃ emissions from lagoons are lower than indicated by current emission factors and a significant fraction of N is emitted as N₂.

There are complex interactions between carbon (C) and N compounds during manure processing by microbial and chemical processes. While little emissions' research for methane (CH₄) and carbon dioxide (CO₂) has been accomplished (Sharpe et al. 2001; DeSutter and Ham 2005) in AFOs, Harper et al. (2000; Table 1; 2010) found interesting correlations between emissions of NH₃, CH₄, nitrous oxide (N₂O), and CO₂ from manure-processing lagoons. These and other studies (Harper et al. 2010) show that manure management aimed at reducing the emissions of one gas could have the undesired consequence of increasing emissions of other gases. In these studies, manure lagoons with a high rate of methanogenesis also converted significant amounts of ammonium (NH₄⁺) to benign N₂ gas with little or no N₂O produced [in the lagoons with the highest rate of methanogenesis, atmospheric N₂O was actually absorbed by the lagoon (Harper et al. 2000)]; however, when methanogenesis decreased, smaller emissions of N₂ occurred and higher rates of N₂O were produced. Harper et al. (2010) also showed that removing organic material from swine production farms for biogas production reduced CH₄ emissions by 47 % (the reduction resulted in a 44 % decrease in radiative forcing gases) from the biogas farms while increasing NH₃ emissions from the biogas farms by 46 %, a substantial increase in air-quality emissions. Weaver et al. (2012) also showed similar results. The above studies suggest there is a relationship between the amount of methanogenesis and conversion of NH₄⁺ to N₂ gas in manure-processing lagoons. Thus, the main purpose of this study was to measure biological gas emissions from six manure-processing lagoons within a three-county area of eastern NC, a farm in GA, and in a large swine operation in the CGB (15 farms), and to evaluate the relationship between methanogenesis (CH₄ production) and conversion of organic and inorganic N to N₂ gas (N₂ production).

Table 1 Summary of lagoon ebullition studies for methane, carbon dioxide, and dinitrogen gases used in this report

Study location	Study period	Farm type	Lagoon size (ha)	Number animals	Average weight of animals (kg)	Feed N input (kg N Farm ⁻¹ d ⁻¹)	Feed input per surface area (kg feed d ⁻¹ ha ⁻¹)	Lagoon ammonium (mg NH ₄ ⁺ -N L ⁻¹)	CH ₄ emissions (kg CH ₄ ha ⁻¹ d ⁻¹)	CO ₂ emissions (kg CO ₂ ha ⁻¹ d ⁻¹)	N ₂ emissions (kg N ₂ ha ⁻¹ d ⁻¹)
NC (20) ^a	1999–2001	FW #1 ^b	2.26	2,000	196.6	117	2,227	175	26.2	0.8	10.2
NC (2149)	1999–2001	FW #2	1.09	1,350	237.0	136	4,960	389	100.3	5.8	25.8
NC (318)	1999–2001	FW #3	0.69	7,644	61.3	111	6,827	422	103.7	5.3	16.4
NC (2704)	1999–2001	F #1	1.61	2,400	197.0	148	4,338	348	73.3	3.2	18.5
NC (3101)	1999–2001	F #2	0.77	3,248	61.3	127	6,205	427	107.3	4.8	17.8
NC (10)	1999–2001	FF	2.55	1,200	643.3	502	7,247	545	169.8	21.7	43.8
CGB (1, 2, 3) ^c	2002–2003	S	1.93	5,000 ^d	185.0 ^d	423 ^d	9,500 ^e	1,081	74.8	17.5	36.0
CGB (4, 5, 6) ^c	2002–2003	N	0.50	12,000 ^d	13.6 ^d	102 ^d	8,900 ^e	1,475	71.4	20.5	18.2
CGB (7, 8, 9) ^c	2002–2003	F	1.69	11,520 ^d	68.0 ^d	442 ^d	11,400 ^e	1,851	72.1	20.2	21.2

The following published emissions from GA (Harper et al. 2000) and CGB (Weaver et al. 2012) were compared in this study:

GA (1)	1994–1998	F	NA ^f	NA	NA	NA	NA	NA	125.8	7.3	23.1
CGB (10, 11, 12) ^e	2004–2006	F(B) ^g	1.69	10,187	85.0	399	10,800	1,725	87.0	34.5	16.7
CGB (13, 14, 15) ^e	2004–2006	F(C) ^g	1.69	11,954	78.0	399	10,800	1,752	95.7	36.8	20.3

^a Farm number in parentheses

^b Letters represent: F Farrow, FW Farrow-to-Wean, S Sow, N Nursery

^c Average of three farms

^d Estimated from Harper et al. (2006)

^e Calculated from feed N input and 2.3 % N in feed

^f NA not applicable, four cascading lagoons

^g Biofuel (B) and control (C) farms

Materials and methods

In the 22 swine lagoons studied from all regions, undecomposed organic material (manure) from animal production houses is pumped to lagoons where the organic materials settle to the bottom forming a layer of semi-solid organic material which is anaerobically decomposed producing gas. Gas bubbles emitted from the sludge layer in each of the lagoons, were trapped in six collectors (Fig. 1) randomly located within each of six areas of the lagoon. These gas collectors do not interfere with the emission process, as with NH_3 chambers (Harper, 2005). On a short-term basis ($< \sim 2$ weeks), ebullition gases, the result of biological and thermodynamic processes, are emitted from the lagoon bottom and are not affected by climatic events at the lagoon surface; however, NH_3 emissions are highly influenced by the physical processes of water surface turbulence and temperature. The collectors were made of 20-L, open-bottom carboys (0.275 m diameter) with flotation collars at the top of the carboys (Fig. 1) and tethered to the lagoon bottom to collect the mass-flow gases (bubbles) before they reached the water–air interface. All air was removed from the collectors at placement. Water in the collectors was displaced by the ebullition gases over time, visually measured on a graduated scale on the collector periodically to determine gas mass-flux. Gases were transferred from the collectors using sample lines flushed with the gases from the collectors and then subsequently attached to evacuated six-L SUMMA canisters. The SUMMA canister samples were then transported to a laboratory where gas samples were analyzed by gas chromatography (Harper et al. 2004b; Weaver et al. 2012). No N_2O was found in the collectors via GC. In other studies no N_2O emissions were found from anaerobic lagoons using atmospheric transport techniques and tunable diode laser spectroscopy (Harper et al. 2000, 2004a, b). Samples of helium (He) injected into the collectors showed a sampling procedure error of about 1 % due to atmospheric N_2 contamination (see Harper et al. 2004b). Further, modeling studies showed the theoretical maximum contamination from the atmosphere would be <5 – 10 % (De Visscher and Harper 2005, unpublished data). Gas fluxes were determined by measuring the amount of gases collected divided by the time between measuring intervals (collection volumes were measured as ebullition

necessitated, normally from two to three times per week in summer and weekly or bimonthly in winter) and then multiplying the emissions by the measured concentrations of each gas. This sampling protocol has been used extensively and further description of the measurement technique may be found in Harper et al. (2000, 2004b) and Weaver et al. (2012).

A summary of all farms in this study is included in Table 1. Fifteen farms of four different types in the CGB were sampled during 2002–2006: two sets (2002–2003 and 2004–2006) of three each F farms; another set of three F farms with organic matter removed for biogas production (2004–2006); one set of three each of nursery (N) farms (2002–2003) and sow (S) farms (2002–2003). Data from 2004 to 2006 are from an earlier published study (*after* Weaver et al. 2012). Six farms were sampled during 1999–2001 for N and C emissions in NC including three farrow-to-wean (FW), two finisher (F), and one farrow-to-finish (FF) farms. Data from an F farm in GA during the period of 1994–1998 were included (*after* Harper et al. 2000). Farm animal numbers ranged from 1,400 to 12,000.

Farms were selected in three geographical areas: fifteen in the CGB, six in three NC counties, and one in GA, to evaluate the effect of management on biogas emission rates (subject to host availability). The farm types included F, FW, and FF farms with input feed protein ranging from 13 to 17 % (feed N from 2.1 to 2.7 %). Three sow farms in the CGB were selected for comparison to production farms. Feed input, feed analysis, animal numbers and weights, number of animals sold, and other management information were supplied by the host owners/managers where available. Lagoon temperature was measured 2.5 cm below the water surface and within the sludge layer with micro temperature-loggers [Onset Computer Corp, Bourne, ME (Note: commercial names are included for the benefit of the reader and do not imply endorsement by the authors or their host institutions)]. The lagoons typically never formed crusts on the surface and were well mixed as demonstrated by near uniform temperatures from the top to the top of the sludge layer in lagoons of the CGB study. Since it is not appropriate to calculate NH_3 emissions from chamber systems (Harper 2005), lagoon NH_3 emissions were calculated from pH, NH_4^+ measurements of effluent samples (collected in bottles at the surface of each lagoon), surface lagoon temperatures, and

wind speeds measured at 1.5 m height (from a meteorological station on site), and a lagoon NH_3 emissions model by De Visscher et al. (2002). Housing NH_3 emissions were estimated from a model developed by Harper et al. (2004a) for North Carolina swine farms.

Effluent and sludge layer samples collected were frozen immediately and shipped to a laboratory for analysis of NH_4^+ , nitrate (NO_3^-), nitrite (NO_2^-), and pH (for a description of analysis procedures see Harper et al. 2000, 2006). All lagoons were sampled similarly on a monthly basis.

The precision of biogas emission measurement was evaluated using the absolute value of the coefficient of variation, or relative standard deviation (RSD), obtained by dividing the standard deviation by the mean. To evaluate precision of the individual carboy measurements, the daily carboy emissions of the six lagoon carboys were used to calculate the daily average for the lagoon along with its RSD. The daily RSDs of the lagoons were averaged to calculate the average daily RSD and standard deviation of the daily RSD. To evaluate the precision of the farm lagoon emissions, a similar procedure was followed. Individual farm lagoon emissions are the average of the six carboy measurements. As lagoon emissions from three identical farms were measured for each farm type, the average individual farm emissions per farm type could be determined as well as the standard deviation of the individual farm emissions to calculate daily, monthly and yearly RSDs for each farm type. The RSDs for each farm type were averaged and a standard deviation was subsequently determined for daily, monthly and yearly RSD of individual farm emissions.

Results and discussion

Precision of biogas emission measurements

Average annual gas emissions (total component and percent of total) increased as the amount of farm input-feed per size-of-lagoon increased (i.e. increased manure C with respect to lagoon processing size). Biogas production varied substantially among the six collectors on each lagoon site. The RSD between collectors on a single lagoon, on a daily basis, was 48 ± 13 %. While there was considerable variability between individual collector's measurements, the



Fig. 1 Gas collectors constructed from open-bottom 20-L carboys. Graduations for evaluation of gas volumes located on the side of the carboy

variability of biogas emissions measurements was much less between lagoons when the six collectors were averaged. For example, the average RSDs of lagoon daily biogas emissions (average of six collectors) from lagoons of identical farms in the CGB were 23 ± 2 %. The variability of measurements between identical farms decreased even further when compared on a monthly (average RSD = 14 ± 6 %) or yearly basis (8.8 ± 6.0 %). We interpret this to mean that the 6 collectors are adequate to determine representative emission measurements on a yearly basis. Individual gas emissions showed regression relationships vs. feed input (R^2) greater than 0.67 for total component emissions (Fig. 2a) and greater than 0.86 for percent of all component gas emissions versus feed input (Fig. 2b).

Climate/temperature effects

When comparing biogas production between farms, temperature effects in the lagoon sludge must be considered. Farms from the CGB were included to test

the robustness of the trends in biogas production and their relationship to feed input and temperature. Each system monitored in the CGB was comprised of three identical farms allowing for quantification of the variance in the data. Average monthly CH_4 production was directly related to sludge (where most of the processing occurs) temperature (Fig. 3a). On an annual basis, measured sludge temperatures were found to be within one degree ($0.8\text{ }^\circ\text{C}$ higher) of the average annual air temperature at 1.5 m height (Harper and Weaver, unpublished data), and we suggest that air temperature can be used as a surrogate temperature for the sludge. When CH_4 production was plotted versus average monthly air temperature (Fig. 3b), the gas production dependence upon monthly air temperature was almost as good as sludge temperature (R^2 values similar). Additionally, the dry climate of the CGB causes much higher evaporation rates and results in different management of swine lagoons.

Feed input effects

Data from the NC farms were used to test for the effects of feed input on biogas production. The NC data demonstrated that total biogas emissions ($\text{kg gas ha}^{-1}\text{ d}^{-1}$) increased linearly (Fig. 2a) with daily feed input per lagoon size ($\text{kg feed d}^{-1}\text{ ha}^{-1}$) ($R^2 = 0.67$). Component gas emissions all increased linearly with feed input but CH_4 had the largest increase with feed input per lagoon size ($R^2 = 0.78$). Carbon dioxide and N_2 gas emissions also increased linearly but at smaller rates than CH_4 (with correlations of $R^2 = 0.76$ and 0.32 , respectively). Lower correlations for N_2 gas can be partially explained by a change in composition of biogas with feed input (Fig. 2b) where CH_4 and CO_2 emissions, as the percentage of total gas production, increased and N_2 emissions decreased with respect to increased daily feed input rates ($\text{kg feed d}^{-1}\text{ ha}^{-1}$). The N_2 gas produced from the conversion of NH_4^+ to N_2 , was not positively correlated with feed input (as was CH_4 and CO_2) since N_2 is produced via a different mechanism than methanogenesis (Weaver et al. 2012).

Feed input values from the CGB could not be used to predict emissions (using the linear relationships determined in Fig. 2a) in other areas due to large differences in lagoon temperatures and to very different animal and manure management. In the CGB lagoons, no effluent was discharged from the lagoon

system to maintain water levels (evaporation was sufficient); thus, organic matter was diminished only by anaerobic decomposition and all lagoon N was removed either via NH_3 volatilization and/or conversion of NH_4^+ to N_2 gas (Harper et al. 2000, 2004b; Weaver et al. 2012). Harper et al. (2000) found no N_2O emissions from swine anaerobic processing lagoons (indeed, there was absorption of N_2O from the atmosphere by the lagoon). Additionally, because the feed input ($\text{kg feed ha}^{-1}\text{ d}^{-1}$) was similar between lagoons in CGB (Table 1), the relationship between feed input and emissions could not be tested in the CGB.

The relationship between NH_4^+ concentration and gas emissions was evaluated in the NC lagoons. Similar to lagoon biogas emissions in a GA study (Harper et al. 2000), as NH_4^+ concentration increased across the six NC lagoons, total and individual gas emissions increased. However, the increased emissions effect was due to an increase in manure availability resulting in more biological decomposition from more feed input (Fig. 2a). Additionally, NH_4^+ concentrations also increased with more biological decomposition. Consequently, higher NH_4^+ concentrations and gas emissions are both correlated to feed input and not necessarily to each other.

Mechanisms for N_2 production

When Harper et al. (2000) could not balance the feed N input and all forms of N output (including meat, lagoon NH_3 volatilization, field application NH_3 losses, field denitrification losses of N_2 and N_2O emissions, lagoon N_2O emissions, etc.), they suggested the possibility that some of the NH_4^+ may have been converted to N_2 during manure-processing and that different reactions were involved, depending on the N form and concentration. With higher NH_4^+ concentration and biological activity (i.e. CH_4 production) their studies suggested that the N_2 production may have occurred via ‘chemical denitrification’ (Van Cleemput 1997). Thermodynamics and the Gibbs free energy of reaction for chemical denitrification (Van Cleemput 1972) suggest that spontaneous conversion of NH_4^+ to N_2 may occur in animal manure lagoons (Harper et al. 2004b, Table 7). It is possible that there is some biological denitrification in the lagoons, but we think it is small since we measured little NO_3^- ($<0.1\text{ mg NO}_3^-\text{-N L}^{-1}$). Furthermore, dissolved

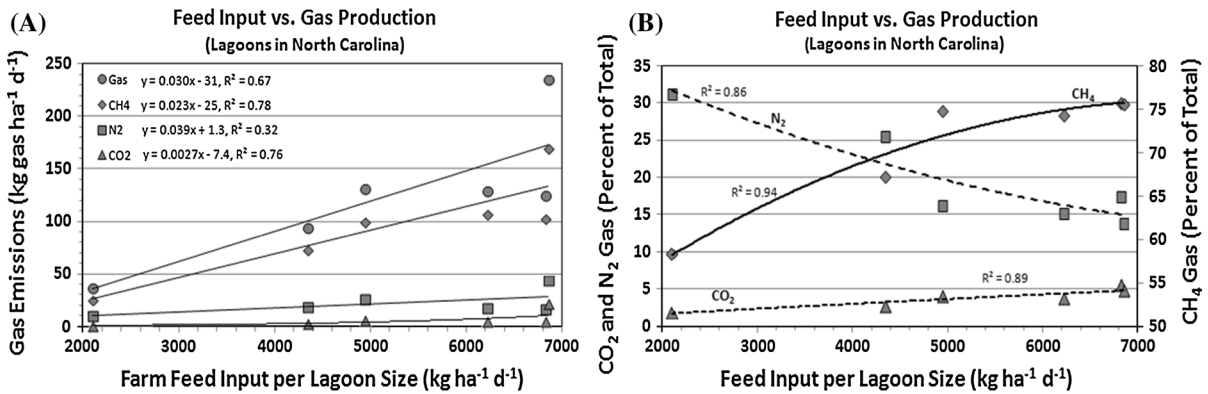


Fig. 2 Average annual lagoon methane, dinitrogen, and carbon dioxide emissions as emissions per unit area of lagoon surface (a) and percent of total gas emissions (b) with respect to feed input per lagoon size in North Carolina

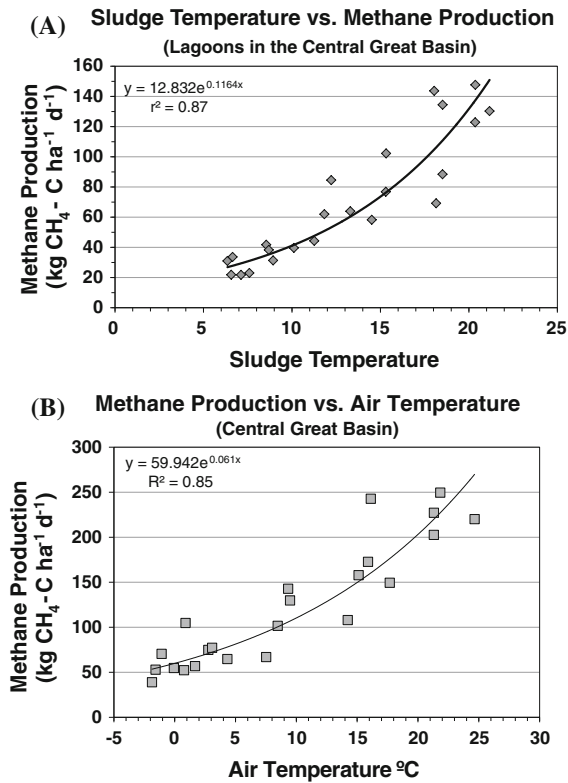


Fig. 3 a Average monthly methane production (of three farms) in relation to the sludge temperature at the bottom of the lagoons (where most of the decomposition occurs) over 2 years in the Central Great Basin (CGB). b Average monthly methane production (of three farms) in relation to the air temperature over 2 years in the CGB

oxygen (O₂) concentrations (mean of about 0.1 % dissolved O₂ across all the primary lagoons) can barely support autotrophic nitrification even under

otherwise optimal conditions. We did not find NO₂⁻, an intermediate step in biological nitrification/denitrification, in any of the primary lagoons. Zhang (2003) in studies of an anaerobic sludge reactor also found almost all nitrite removed (97–100 %) with gas contents of 89, 8, and 3 % of N₂, CH₄, and CO₂, respectively. These and other anaerobic laboratory studies (Harper et al. 2001, unpublished data) showed similar conversion of solution NH₄⁺ to N₂ gas. Studies of swine lagoons by Hunt et al. (2010) found similar conclusions to Harper et al. (2000, 2004) finding little N₂O (produced from incomplete denitrification) being part of the system N balance. They also found there was a lack of sufficient denitrification enzyme activity (DEA) within the wastewater to support large N₂ losses via classical nitrification and denitrification.

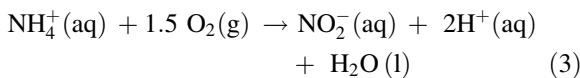
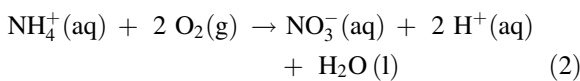
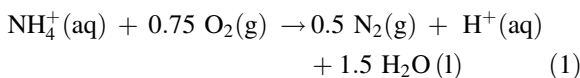
There are other possible microbial processes to explain the N₂ production (Thamdrum 2012). Like classical denitrification and the anaerobic ammonia oxidation bacterial process (ANAMMOX), the full extent of conversion of NH₄⁺ to N₂ remains unclear (Ettwig et al. 2009). Kartal et al. (2011) has recently presented strong evidence to explain the ANAMMOX mechanism for conversion of NH₄⁺ to N₂ production; meanwhile, in this paper we demonstrate that the simple conversion of NH₄⁺ to N₂ is thermodynamically favorable later in the manuscript.

Harper et al. (2000) showed that as lagoon NH₄⁺ increased, NO₃⁻ and dissolved O₂ decreased, while N₂ and CH₄ emissions increased. Other studies have shown that when organic C is removed for biogas production, methanogenesis is reduced and the lagoon NH₄⁺ content is increased (Amon et al. 2005) and

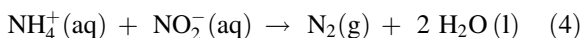
measured whole-farm NH_3 emissions are increased (Harper et al. 2010). The above studies had treatments which reduce methanogenesis or lagoon NH_4^+ concentration but the studies in this research compare emissions from normal animal management and manure processing systems. The three lagoons in which organic matter was removed for biogas production were included to provide an additional comparison for the effect of reducing decomposition and methanogenesis.

Thermodynamic relationships

The net effect of all these studies suggests that as methanogenesis is decreased, conversion of NH_4^+ to N_2 is decreased. We think the causal relationship between methanogenesis and NH_4^+ to N_2 conversion is thermodynamically favored, while competing with other NH_4^+ oxidizing reactions. The following reactions are considered:



Reaction (1) could represent either a chemical denitrification step, or a microbial process. Without more direct evidence no distinction can be made between a chemical and a microbial process. Hence, we simply refer to reaction (1) as a “conversion” without specifying its nature. Reaction (2), or nitrification, is discussed below. Reaction (3) is significant as no appreciable concentrations of NO_2^- were determined in any of the lagoons. The nitrite ion is key for the anaerobic oxidation of NH_3 (ANAMMOX) as NO_2^- must be present [Eq. (4)]:



The Gibbs free reaction energy $\Delta_r G$ of the three reactions was calculated under the following conditions: NH_4^+ concentration 1500 mg L^{-1} , NO_3^- -N concentration 0.1 mg l^{-1} , NO_2^- -N concentration 0.1 mg L^{-1} , pH 8, N_2 partial pressure 81 kPa, O_2 partial pressure $0.1\text{--}10^{-15}$ bar. The calculation is similar to that of

Harper et al. (2004b) except that the speciation between NH_3 and NH_4^+ was not considered (NH_4^+ is the dominant species and its concentration does not influence the relative $\Delta_r G$ between the three reactions).

This relationship is illustrated in Fig. 4. A negative value of $\Delta_r G$ indicates that the reaction is thermodynamically favorable. It is clear that the formation of NO_3^- from NH_4^+ is thermodynamically more favorable than N_2 or NO_2^- formation at O_2 partial pressures above 10^{-8} bar when other concentrations remain the same. At lower O_2 partial pressures N_2 formation is thermodynamically more favorable than the formation of NO_3^- and NO_2^- from NH_4^+ . This might explain why N_2 production and CH_4 production are correlated. Methanogenesis is only possible at extremely low O_2 concentrations, and under these conditions N_2 production is thermodynamically more favorable than NO_3^- production. This should not be interpreted as conclusive evidence, as both reactions are thermodynamically favorable in all conditions considered; and, other factors like kinetics play a role as well. The presence of an electron donor (organic material) removes oxygen to the point where NO_3^- production becomes thermodynamically less favorable than N_2 production. Kinetically, nitrification has an estimated saturation constant of 0.5 mg L^{-1} according to the standard activated sludge model, ASM3 (Gujer et al. 1999). The ASM3 model predicts that nitrifiers cannot maintain their activity at oxygen concentrations below 0.026 mg L^{-1} (6.3×10^{-4} bar) under otherwise optimal conditions (i.e., in the absence of any other limiting factor).

The sensitivity of the thermodynamics of reactions (1) (2), and (3) to the variables that were kept constant in the above analysis was investigated. The sensitivity of $\Delta_r G$ to any of the reactants or products was determined to be less than $11.42 \text{ kJ mol}^{-1}$ for any 100-fold change in concentration (or 2 pH units). It is concluded that the thermodynamics of NH_4^+ oxidation is only slightly sensitive to pH and concentrations of NO_3^- , NO_2^- , N_2 , and NH_4^+ , so a possible uncertainty of any of these variables will not invalidate the analysis.

Comparison of system N emissions

The relative N emissions (ratio of N emitted to feed N input) from the farms in a geographical area (in NC) are shown in Fig. 5 (volatile NH_3 -N from housing and lagoons, NH_4^+ -N conversion to N_2 , protein-N, and unknown-N). Measured N_2 emissions were not

consistent within farm types or across all farm locations. The smallest N₂ flux occurred in a farm (FW #3) which also had the highest estimated housing NH₃ emissions. Inversely, the largest N₂ flux was in a farm (FF) with the smallest housing NH₃ emission losses [housing NH₃ emissions were only slightly linearly correlated with N₂ emissions across all farms, R = 0.63 (R² = 0.40, n = 6)]. Although not conclusive, the inverse relationship suggests that increased N loss as NH₃ will reduce N₂ emissions.

Statistical models for gas emissions

The correlation of methanogenesis and N₂ emissions (R² = 0.78) was quite good across the lagoons studied in NC leading us to consider if the relationship (y = 0.23x) would be comparable across wide geographical regions of the U.S., as well as with management practices. Methane and N₂ emissions were combined (Fig. 6) with the studies in the CGB and from a previous study in GA (Harper et al. 2000). The relationship between CH₄ and N₂ emissions were surprisingly similar changing the overall correlation only slightly, R² = 0.71, and a linear relationship of y = 0.20x, suggesting a near-universal relationship between methanogenesis and conversion of NH₄ to N₂ in highly anaerobic conditions (comparing NC results to all results). The correlation of fluxes was significant at the 2 % level (t = 3.76). A linear relationship can be inferred from the data:

$$F_{N_2} = BF_{CH_4} \tag{5}$$

with F_i the flux of compounds i in kg ha⁻¹ d⁻¹ and B an empirical coefficient. Based on simple linear regression, the value of B = 0.20 is found because of the similar compositions of gas from individual systems.

The S farms were not included in the relationship (see X data point) since the animal size and management, feed input, and manure and urine management were very different.

Gas emissions will vary with respect to farm management (feed input, animal weight, etc.) and climatic conditions. As such, it is difficult to directly compare emissions from different locations. Farm management factors most correlated (and data most likely available) are feed input and size of animal. The climatic

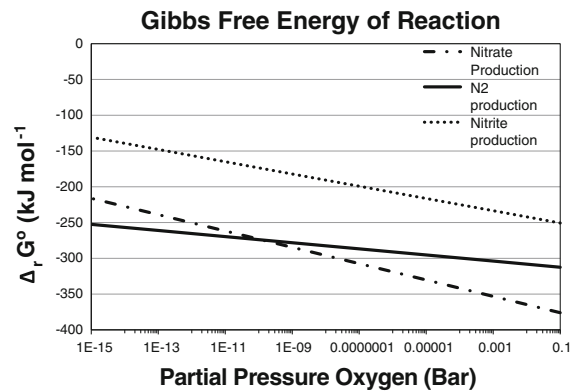


Fig. 4 Gibbs free energy of reaction for N₂ production and NO₃⁻ production from NH₄⁺ versus O₂ partial pressure (NH₄⁺ concentration 1,500 mg L⁻¹, NO₃⁻ concentration 0.1 mg L⁻¹, pH 8, N₂ partial pressure 81 kPa)

factor which most affects the biological decomposition of sludge is the temperature of the biological material in the lagoon anaerobic layer (i.e., sludge temperature, see Fig. 3a). Measurements were used from all the farm systems in the CGB to correct for temperature effects by correlating monthly air temperature with monthly gas emissions as discussed previously. The dependence upon feed input per surface area was estimated from NC data where there was no significant temperature difference between farms. Annual CH₄, N₂, and CO₂ emissions (kg gas component ha⁻¹ d⁻¹) were estimated from lagoons by the following relationships:

$$CH_4 = (0.023 \times FIS - 25) \times (0.039 \times T_a + 0.26) \tag{6}$$

$$N_2 = (0.0039 \times FIS + 1.3) \times (0.033 \times T_a + 0.41) \tag{7}$$

$$CO_2 = (0.0027 \times FIS - 7.4) \times (0.040 \times T_a + 0.24) \tag{8}$$

where FIS is the annual average daily feed input per lagoon surface area (kg feed d⁻¹ ha⁻¹) and T_a is the average annual air temperature (°C) at the site. Temperature corrections were standardized to the average annual air temperature in the NC studies (18.85 °C). When these relationships were used to estimate CGB gas emissions, estimated CH₄ emissions were 74 ± 24 % high, CO₂ emissions were 58 ± 13 % low, and N₂ emissions were 49 ± 42 % high compared to measured emissions.

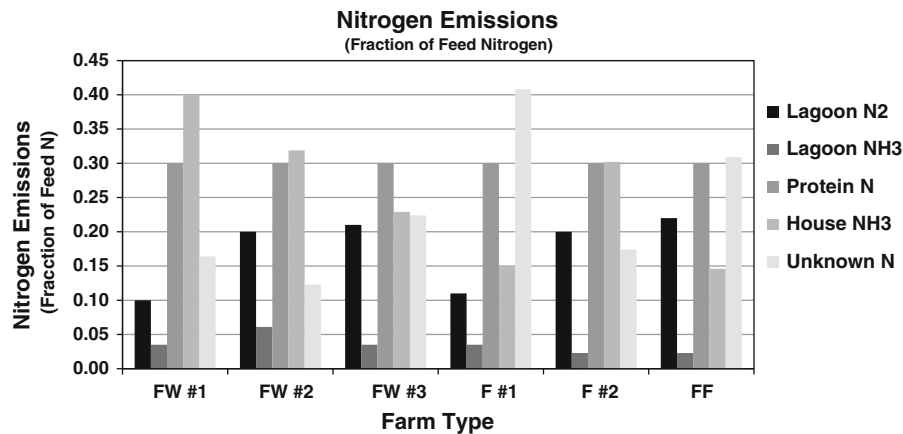


Fig. 5 Comparison of N emissions from farms due to housing NH₃ losses, lagoon NH₃ and N₂ losses, and protein N removal from the farms (*F* finisher, *FF* farrow to finisher, and *FW* farrow to wean)

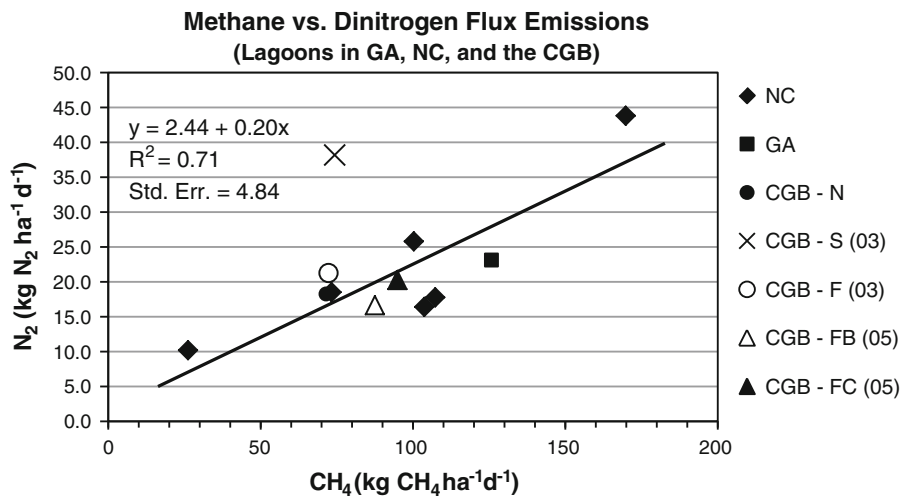


Fig. 6 Average annual dinitrogen production due to anaerobic decomposition in relation to methane production at six farms in North Carolina, 15 in the Central Great Basin (CGB, all data points from the CGB are the average of three identical farms), and one in Georgia (from Harper et al. 2000). The two data

points from CGB–F(05) are from Weaver et al. 2012. The Sow farm in the CGB was not used in the relationship since the animal and waste management systems were very different (see X data point)

Using information on the variables measured, we analyzed the data to determine the variables most related (and possibly causal), not already mentioned, to the conversion of NH₄⁺ to N₂ for the studies in NC. The amount of feed per average animal weight (and C input) had the highest correlation with N₂ emissions ($R^2 = 0.87$). This is not surprising as feed per animal correlates highly with C and N lagoon input (and consequent increased methanogenesis), along with

NH₄ conversion to N₂, across studies over three states (Fig. 6).

Conclusions

In summary, gas emissions were measured in six anaerobic, manure-processing swine lagoons across NC, 15 in the CGB, and one in GA. Conversion of

NH_4^+ to N_2 was observed in all lagoons and a correlation was found between methanogenesis (CH_4 emissions) and conversion of ammoniacal N to benign N_2 gas. Anaerobic digestion not only decomposes organic C to CH_4 , but also organic N to NH_4 conceptually leading to an increase in NH_4 concentration and, as a consequence, a potential increase in NH_3 emissions. However, we find in these studies that a reduction of C causes an *increase* in NH_3 emissions, rather than a decrease, since NH_4 is not converted to N_2 . Dinitrogen emissions were seen to linearly increase with methanogenesis (CH_4 production), further explaining why removal of organic material from lagoons for biogas production would increase NH_3 emissions from lagoons, a phenomenon which has been seen in other studies (Harper et al. 2010; Weaver et al. 2012). A causal effect for the relationship between methanogenesis and the potential conversion of NH_4^+ to N_2 is explained based on thermodynamics. Dinitrogen emissions can be estimated across all regions utilizing CH_4 emissions (if available). The highest correlation between normally-obtained management variables and N_2 emissions was input-feed per animal-weight which provides the organic C for methanogenesis. Simple statistical regression models including average annual feed input and annual average air temperature were developed which explained most of the N_2 emissions variability and had an acceptable error when tested against other lagoons. These studies provide the capability to estimate farm lagoon CH_4 , CO_2 and N_2 emissions from normally-available farm input and local climate data. Further investigations into the mechanisms of NH_4^+ to N_2 conversion and into the variability of CH_4 emissions are needed.

Acknowledgments The authors wish to express their appreciation to the project technical assistants, M.F. Thornton, J. Scarbrough, C. Butler, P. Caddis, L. Mathis, and J. Merritt for their efforts in these studies and to the numerous undergraduate students from SUU for their assistance. Gratitude is expressed to R.R. Sharpe (USDA, *ret.*) for his support in these studies and to P. Rochette and T. Clough for manuscript reviews. A special thanks is extended to the Global Climate Change Program, USDA-ARS; the North Carolina Pork Council; the Utah Pork Council; Smithfield Co.; and to the host swine producers who helped make these studies possible.

Open Access This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

References

- Amon B, Kryvoruchko V, Amon T, Boxberger J (2005) Effects of covering dairy cow slurry during storage on CH_4 , NH_3 , N_2O emissions. *Landtechnik* 60:216–217
- Aneja VP, Chauhan JP, Walker JT (2000) Characterization of atmospheric ammonia emissions from swine waste storage and treatment lagoons. *J Geophys Res* 105:11535–11545
- Blunden J, Aneja VP (2008) Characterizing ammonia and hydrogen sulfide emissions from a swine waste treatment lagoon in North Carolina. *Atmos Environ* 42:3277–3290
- Cohen AJ, Anderson HR, Ostro B, Pandey KD, Krzyzanowski M, Künzli N, Gutschmidt K, Pope A, Romieu I, Samet JM, Smith K (2005) The global burden of disease due to outdoor air pollution. *J Toxicol Environ Health* 68:1301–1307
- De Visscher A, Harper LA, Westerman PW, Sharpe RR, Van Cleemput O (2002) Ammonia emissions from anaerobic swine lagoons: model development. *J Appl Meteorol* 41:426–433
- DeSutter TM, Ham JM (2005) Lagoon-biogas emissions and carbon balance estimates of a swine production facility. *J Environ Qual* 34:198–206
- Doorn MRJ, Natschke DF, Meeuwissen PC (2002a) Review of emission factors and methodologies to estimate ammonia emissions from animal waste handling. U.S. Environmental Agency Rept. EPA-600/R-02-017, April, 2002. U.S. Environmental Protection Agency, Washington, DC
- Doorn MRJ, Natschke DF, Thorneloe SA, Southerland J (2002b) Development of an emission factor for ammonia emissions from US swine farms based on field tests and application of a mass balance method. *Atmos Environ* 36:5619–5625
- Ettwig KF, Van Alen T, Van De Pas-Schoonen KT, Jetten MSM, Strous M (2009) Enrichment and molecular detection of denitrifying methanotrophic bacteria of the NC10 phylum. *Appl Environ Microbiol* 75:3656–3662
- Gujer W, Henze M, Mino T, van Loosdrecht M (1999) Activated sludge model no. 3. *Water Sci Technol* 39:183–193
- Harper LA (2005) Ammonia: Measurement Issues. In: J.L. Hatfield and J.M. Baker. (eds.) *Micrometeorological Measurements in Agricultural Systems*. Agron Monogr 47, ASA, CSSA, and SSSA, Madison WI p. 345-379
- Harper LA, Sharpe RR (1998) Ammonia emissions from swine waste lagoons in the Southeastern U.S. Coastal Plains; Final Grant report to Division of Air Quality, North Carolina Department of Environment and Natural Resources, Raleigh, NC, USDA-ARS Agreement No. 58-6612-7 M-022, December 1998. USDA-ARS, Watkinsville, GA, 1998
- Harper LA, Sharpe RR, Parkin TB (2000) Gaseous nitrogen emissions from anaerobic swine lagoons: ammonia, nitrous oxide, and dinitrogen gas. *J Environ Qual* 29:1356–1365
- Harper LA, Sharpe RR, Simmons JD (2004a) Ammonia emissions from swine houses in the southeastern United States. *J Environ Qual* 33:449–457
- Harper LA, Sharpe RR, Parkin TB, De Visscher A, Van Cleemput O, Byers M (2004b) Nitrogen cycling in swine production systems: ammonia, nitrous oxide, and dinitrogen gas emissions. *J Environ Qual* 33:1189–1201

- Harper LA, Weaver KH, Dotson RA (2006) Ammonia emissions from swine waste lagoons in the Utah Great Basin. *J Environ Qual* 35:224–230
- Harper LA, Flesch TK, Weaver KH, Wilson JD (2010) The effect of biofuel production on swine farm ammonia and methane emissions. *J Environ Qual* 39:1984–1992
- Harper LA, Denmead OT, Flesch TK (2011) Micrometeorological techniques for measurement of greenhouse gas emissions from ruminant animal production. *Anim Feed Sci Tech* 166(167):227–239
- Hatfield JC, Brumm MC, and Melvin SW (1993) Swine manure management. In: *Agricultural Utilization of Municipal, Animal, and Industrial Waste*, USDA-ARS, Washington, DC, 1993 p. 40–57
- Hunt PG, Matheny TA, Ro KS, Vanetti MB, and Ducey TF (2010) Denitrification in anaerobic lagoons used to treat swine wastewater. *J Environ Qual* (published online, doi:10.2134/jeq2009.0385)
- Kartal B, Maalcke WJ, de Almelda NM, Cirpus I, Gloerich J, Geerts W, Op den Camp HJM, Harhangt HR, Janssen-Megens EM, Francois K, Stunnenberg HG, Keltjens JT, Jetten MSM, Strous M (2011) Molecular Mechanism of anaerobic oxidation. *Nature* 479:127–130
- Pope CA III, Burnett RT, Thun MJ, Calle EE, Krewski D, Ito K, Thurston GD (2002) Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. *J Am Med Assoc* 287:1132–1141
- Rochette P, Gregorich EG, Desjardins RL (1992) Comparison of static and dynamic closed chambers for measurement of soil respiration under field conditions. *Can J Soil Sci* 72:605–609
- Shah SB, Westerman PW, Arogo J (2006) Measuring ammonia concentrations and emissions from agricultural and liquid surfaces: a review. *J Air Waste Manage Assoc* 56:945–960
- Sharpe RR, Harper LA, Simmons JD (2001) Methane emissions from swine houses in North Carolina. *Chemosphere-Global Change Sc.* 3:1–6
- Thamdrup B (2012) New pathways and processes in the global nitrogen cycle. *Ann Rev Ecol Evol Syst* 43:407–428
- USEPA (2004) *National Emission Inventory—Ammonia Emissions from Animal Husbandry Operations* Draft Report, January 30, 2004. Report found at <http://www.epa.gov/ttn/chief/ap42/ch09>
- Van Cleemput O (1972) Het Denitrifikatieproces in De Bodem. (The denitrification Process in Soil). Ph.D. Thesis, Faculty of Agricultural and Applied Biological Sciences, University of Ghent, Ghent, Belgium, 1972. (in Flemish)
- Van Cleemput O (1997) Subsoils: Chemical and biological denitrification, N₂O and emissions. Proc. Intern. Workshop on dissipation of N from the human N-Cycle and its role in present and future N₂O emissions to the atmosphere. Agr Univ. Of Norway, Oslo. May 22–25, 1997. (No page numbers)
- Weaver KH, Harper LA, Brown SM (2012) Effects on carbon and nitrogen emissions due to swine manure removal for biofuel production. *J Environ Qual* 41:1371–1382