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The effect of biogas ebullition on ammonia emissions from animal manure–processing lagoons

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Abstract

Various models have been developed to determine ammonia (NH_3) emissions from animal manure–processing lagoons to enable relatively simple estimations of emissions. These models allow estimation of actual emissions without intensive field measurements or "one-size-fits-all" emission factors. Two mechanisms for lagoon NH_3 emissions exist: (a) diffusive gas exchange from the water surface and (b) mass-flow (bubble transport) from NH_3 contained within the ebullition gas bubble (as it rises to the surface) produced from anaerobic decomposition of organic matter. The purpose of this research is to determine whether gas ebullition appreciably affects NH_3 emissions and therefore should be considered in emissions models. Specifically, NH_3 mass-flow emissions were calculated and compared with calculated diffusive NH_3 emissions. Mass-flow NH_3 emissions were evaluated based on a two-film model, in connection with the acid dissociation constant of ammonium, to predict the degree of NH_3 gas saturation within the bubbles. Average daily ammoniacal nitrogen concentration, pH, and measured biological gas production (ebullition) in conjunction with literature values for Henry's law constant were used to calculate emissions from NH_3 saturation of ebullition gases. Ebullition enhancement of NH_3 surface emissions due to increased turbulence was estimated from average lagoon ebullition rates and literature values of turbulence enhancement. Ebullition enhancement of NH_3 surface emissions and ebullition mass-flow NH_3 emissions was determined to be <10% and <0.052%, respectively, of total NH_3 emissions. Therefore, because ebullition effects are small, they may be neglected when developing process models to estimate NH_3 emissions from water surfaces of swine manure processing lagoons.

1 | INTRODUCTION

In addition to methane (CH_4) and carbon dioxide (CO_2), ammonia (NH_3) is an emitted gas from confined animal feeding operations, partially from the decomposition of animal manure that occurs in animal manure processing and storage lagoons (USEPA, 2004). As the only significant basic gas found in the atmosphere, NH_3 reacts with acidic gases in the atmosphere to produce aerosol particles that may be detrimental to human health. In addition, these particles may enter ecosystems as precipitation deposition (Asman et al., 1998)

Abbreviations: VS, volatile solids.

and be involved in eutrophication (Portejoie et al., 2002). The amount of NH_3 emitted by agriculture is thought to be significant (Battye et al., 1994; Bouwman et al., 1997). To be able to address this issue, the amount of NH_3 emitted must be properly characterized.

Various methods have been developed to quantify NH_3 emissions from confined animal feeding operations. One such method involves using models to estimate NH_3 emissions of storage/processing lagoons (Aneja et al., 2001; Arogo et al., 1999; Bajwa et al., 2006; De Visscher et al., 2002; Grant et al., 2013; Harper et al., 2004, 2019,; Liang et al., 2003; Teye & Hautala, 2008; Zhang et al., 1994). To properly develop models to predict NH_3 emissions, the mechanisms that affect NH_3 emissions must be understood.

When predicting NH_3 emissions from a lagoon, two exchange mechanisms of transfer between the water and the atmosphere should be considered: (a) diffusive gas exchange due to turbulent transport of the NH_3 from the water surface (surface transport) and (b) mass-flow of NH_3, which is contained within the ebullition bubbles of gas produced from anaerobic decomposition of organic matter in the sediment layer (bubble or ebullition transport). These processes can be modeled provided that a number of assumptions are met. De Visscher et al. (2002) produced an NH_3 volatilization model from manure-management lagoons that closely simulated actual measurements of NH_3 emissions based on non-interference micrometeorological measurements (Harper et al., 2000, 2004, 2019). The De Visscher et al. (2002) model did not account for mass-flow of NH_3 trapped in the anaerobic gas bubbles emitted from the sediment in their mathematical development, having determined the emissions by this method were insignificant. However, Ro et al. (2008) demonstrated enhanced laboratory NH_3 emissions from an ammonium hydroxide (NH_4OH) solution bubbled with compressed air. They measured the concentration of NH_4OH in solution versus time and compared the concentration change with that of an identical control solution that was not bubbled with compressed air. The difference in concentration changes represented differences in NH_3 emission rates. Ro et al. (2008) did not specifically attribute the increase in emissions to either the presence of bubble transport or to an increase or enhancement of surface diffusive transport.

The effect of ebullition on each process needs to be understood to be able to integrate or discount biogas ebullition in NH_3 emission models. Bubble transport can be understood by taking advantage of earlier work (Harper et al., 2000, 2004, 2014; Weaver et al., 2012) done to characterize biological decomposition gas emissions occurring in lagoons. These earlier studies determined not only the composition of the gases but also the daily ebullition rates averaged on a monthly basis. Knowledge of these ebullition rates and the concentration of NH_3 in the bubbles allows for a simple calculation of the bubble transport of NH_3 emissions.

Core Ideas

- Ammonia emissions models are used to estimate emissions from manure processing.
- Ebullition mass transport is insignificant compared with diffusion/turbulence emissions.
- Ebullition surface emission enhancement is less than the error of emission models.
- Biogas ebullition does not need to be included in ammonia emission models.

Although biological decomposition of animal manure in treatment lagoons results in CH_4 and CO_2 emissions (and small amounts of other gases), studies have shown significant amounts of chemical (thermodynamic) conversion of $NH_4{}^+$ to dinitrogen (N_2) gas in lagoons in the U.S. southeastern Coastal Plains and in the Central Great Basin of Utah (Harper et al., 2000, 2004, 2014; Weaver et al., 2012). All of these gases are emitted from the sediment layer and rise to the surface either as small gas bubbles or as an occasional large gas "breakthrough" bubble from the sediment layer where a large single emission may occur. To quantify the amount and components of bubble transport emissions, for these studies, collectors were placed just below the water surface uniformly throughout the lagoons to representatively sample the biogas emissions.

Other researchers have demonstrated that ebullition enhances mass transfer rates across phase boundaries. Monteith et al. (2005) showed that the rate of absorption of NH_3 over an acidic solution increased when bubbling air into the acidic solution occurred versus no bubbling. Huisman et al. (1990) showed that the transfer of aqueous anions to ion exchange particles was enhanced proportional to the gas flux (ebullition) rate. Additionally, Blanes-Vidal et al. (2011) reported increased accuracy in predicting emissions by accounting for ebullition when modeling NH_3 emissions after surface disturbances. Because mass transfer enhancement, due to bubbling, is dependent on the ebullition rate, ebullition rates of observed enhancement in simulated or laboratory studies must be equal to observed ebullition rates in working lagoons in order to predict the actual amount of enhancement in lagoons.

In addition to the submerged chambers (Harper et al., 2000, 2004, 2006, 2014; Weaver et al., 2012), there have been several methods used to directly determine ebullition rates of lagoons using enclosure-type measurements on slurry tanks, slurry ponds, and simulated water bodies. These methods can be classified as either "floating chambers" or "flux chambers." Floating chambers are similar to the submerged containers that must be reset manually; however, in these devices, the biogas is collected in the chamber, and the volume of gas is allowed to escape through a single exit where the flow rate is measured (Craggs et al., 2008; DeSutter & Ham, 2005; Safley & Westerman, 1988). Flux chambers also float on the surface of the water where NH_3 and CH_4 free gas is forced through the chambers and the gas concentrations of CH_4 and CO_2, the main constituents of biogas, entering and leaving the chambers are measured. The flow rate of the gas forced through the chambers, combined with the concentration differences, allows for calculation of biogas ebullition rates (Borhan et al., 2011; Husted et al., 1994; Minato et al., 2013). Very few of either of these enclosure-type measurements have been made on swine lagoons.

Ammonia is a diffusive gas that may have a high partial pressure in the lagoon water depending on the ammoniacal nitrogen concentration ([AN], where $[AN] = [NH_4^+] + [NH_3]$) in solution, the pH, and the solution temperature. It is important to determine how biogas ebullition affects NH_3 emissions because dissolved NH_3 may transfer into and be transported in the gas bubbles released from the sediment layer as they travel through the lagoon solution to the air–water surface layer. Other studies have suggested that the biogas ebullition process may increase turbulence at the lagoon surface and enhance emissions (Monteith et al., 2005; Ro et al., 2008). The purpose of this study was to determine if biogas ebullition has a significant effect on total NH_3 emissions due to entrainment in the escaping bubbles and/or to turbulence at the surface at normal ebullition rates for processing lagoons.

2 | MATERIALS AND METHODS

The swine production units studied are located in the Coastal Plains of North Carolina and the Central Great Basin of Utah (Harper et al., 2004, 2006; Weaver, 2012). The manure disposal system in each case is an anaerobic lagoon; animal house manure is emptied directly into the lagoon. The North Carolina facility is a 1,200-sow farrow-to-finish operation with a 2.7-ha lagoon for manure management. The operating depth of the North Carolina lagoon is 3.1 m with dimensions of 256 m by 85 m, with the long axes in a north-south direction. The Utah facility was a 12,000-head finishing operation with a 1.69-ha (8-m-deep) primary lagoon (it also has a 0.59-ha secondary lagoon that was not a part of this study).

Spatial sampling of lagoon nutrient content, both horizontally (in three locations) and vertically (at the surface and in the sludge layer), was accomplished using a remotely actuated, closed sampler to obtain samples representative of each of the vertical layers. The sample containers were lowered from a boat to the appropriate depths, opened for sample collection, and then closed before bringing them to the surface for sample retrieval and storage. The samples were frozen immediately and shipped to a laboratory for analysis of NH_4^+ and pH (for a description of analysis procedures, see Harper et al. [2000]).

Water temperature was measured at the surface with thermocouples (about −3 cm). Windspeed was measured using cup anemometers (Thornthwaite) at 1.26 m above the lagoon surface mounted on a floating barge sunk 0.05 m below the water surface (for further details see Harper et al. [2000]). When measurement data were not available, wind speed data from a nearby weather station were used.

2.1 | Model development of bubble transport emissions

The mass-flow calculation is based on the model of De Visscher et al. (2002) that describes diffusive NH_3 emissions from anaerobic swine lagoons, which is based on a two-film model in connection with NH_3/NH_4^+ acid base equilibria. The NH_3 emissions within bubbles (mass transport), $E_{b,NH3}$, is given by the relationship

$$E_{b,NH_3} = F_b \cdot C_{bNH_3} \tag{1}$$

where F_b is the volume of the bubbles emitted per m^2 of lagoon surface per day ($m^3\ m^{-2}\ d^{-1}$), and $C_{b,\,NH3}$ is the gaseous bubble concentration of NH_3 (mol m^{-3}).

The concentration of NH_3 in the bubbles can be calculated by understanding the mass transfer between the bubble and its liquid surroundings. Mass transfer between a bubble and its surroundings is proportional to a mass transfer coefficient, $k_{L,b,NH3}$, which is different from the $k_{L,NH3}$ value at the lagoon surface. Based on this bubble mass transfer coefficient, $k_{L,b\ NH3}$, the mass transfer is given by

$$V_b \frac{dC_{b,NH_3}}{dt} = k_{L,bNH_3} A_b \left(C^*_{w,\,NH_3} - C_{w,\,NH_3} \right) \tag{2}$$

where A_b is the bubble surface area, $C_{w,NH3}$ is the concentration of NH_3 in the liquid, $C^*_{w,NH3}$ is the liquid concentration of NH_3 that would be in equilibrium with NH_3 gas in the bubble, V_b is the bubble volume, and t is time. The $C^*_{w,NH3}$ and $C_{b,NH3}$ are connected by Henry's law:

$$H = \frac{C_{b,NH_3}}{C^*_{w,\,NH_3}} \tag{3}$$

where H is the Henry's law constant. Rather than use the concentration of the liquid to predict the mass transfer, the concentration of NH_3 gas in the bubble may be used. The bubble gas concentration ($C_{eq,NH3}$) that would be in equilibrium with the liquid phase concentration ($C_{w,NH3}$) is again given by Henry's law:

$$H = \frac{C_{eq,NH_3}}{C_{w,NH_3}} \tag{4}$$

Equation 2 combined with Equations 3 and 4, assuming a constant bubble volume, leads to the following result:

$$V_b \frac{dC_{b,NH_3}}{dt} = k_{L,b,NH_3} A_b \left(\frac{C_{b,NH_3} - C_{eq,NH_3}}{H} \right) \tag{5}$$

Because $V_b = \pi d_b^3/6$ and $A_b = \pi d_b^2$, where d_b is the bubble diameter, Equation 5 can be rewritten as

$$\frac{dC_{b,NH_3}}{dt} = \frac{6k_{L,b,NH_3}}{Hd_b} \left(C_{b,NH_3} - C_{eq,NH_3} \right) \tag{6}$$

Therefore, the solution of this equation is

$$C_{b,NH_3} - C_{eq,NH_3} = \left(C_{b,NH_3,0} - C_{eq,NH_3} \right) \exp\left(\frac{6k_{L,b,NH_3}}{Hd_b} t \right) \tag{7}$$

where $C_{b,NH3,0}$ is the concentration of NH_3 in the bubble at its production, and t is the time required to rise from the lagoon bottom to the lagoon surface. We define f, a dimensionless quantity, as the measure of the non-equilibrium between the bubble contents and the surrounding liquid:

$$f = \frac{C_{b,NH_3} - C_{eq,NH_3}}{C_{b,NH_3,0} - C_{eq,NH_3}} \tag{8}$$

Thus

$$f = \exp\left(-\frac{6k_{L,b,NH_3}}{Hd_b} t \right) \tag{9}$$

when $f = 0$, the gas bubble is at equilibrium with the surrounding liquid; when $f = 1$, no mass transfer between the bubble and the surrounding liquid has occurred.

Using the bubble rise velocity of 0.17 m s^{-1}, calculated in the appendix (Equation A6), the rise time was found to be 18 s for a typical lagoon depth of 3.1 m. The mass transfer coefficient calculated to be 1.1×10^{-4} m s^{-1} (see Appendix, Equation A1), the dimensionless Henry's constant was taken to be 7×10^{-4} (Montes et al. [2008] reviewed values from 5 to 9×10^{-4} for NH_3), and $d_{b,}$ was estimated at 0.0025 m (Ostrovsky et al., 2008). This leads to a value of f equal to $10^{-3,000}$, which is practically equal to 0, clearly indicating equilibrium. Even with lowering the rise time to 7 s, decreasing $k_{L,b,NH3}$ to 6×10^{-5} m s^{-1}, increasing the bubble diameter to 0.004 m, and increasing Henry's constant by two orders of magnitude, the calculated value of f only increases to 8.9×10^{-11}, which still indicates that the NH_3 in the bubbles is at equilibrium with the surrounding liquid by the time the bubbles reach the surface. The state of equilibrium for NH_3 between the liquid and the bubble allows for the bubble concentration to be calculated using Henry's law from Equation 4.

The concentration of aqueous NH_3 ($[NH_3]_{aq}$ or $C_{w,NH3}$) is calculated from [AN] from the following equation:

$$[NH_3]_{aq} = [AN] \left(\frac{K_a}{K_a + [H^+]} \right) \tag{10}$$

where K_a is the acid dissociation constant of $NH_4{}^+$, and $[H^+]$ is the hydrogen ion concentration calculated from the pH. Equation 10 combined with Equation 4 is used to calculate the bubble-phase NH_3 concentration from the concentration of free NH_3 in the lagoon liquid. This bubble NH_3 (g) concentration is simply multiplied by the gas-bubble flux (per surface area per time) to obtain the NH_3 emissions (per surface area) through bubble ebullition. The total NH_3 (surface) emissions were calculated with the model of De Visscher et al. (2002), which calculated surface emissions and was verified by non-interference micrometeorological measurements of total lagoon NH_3 emissions.

3 | DISCUSSION

Table 1 gives time periods during August 1997 for North Carolina and August 2004 for Utah when the largest emissions of NH_3 volatilization occurred and when ebullition rates are near the highest. Average daily $NH_4{}^+$, pH, and windspeed for the period were used because the ebullition measurement by the gas collectors averaged the gas bubble emissions over this period. Using the lagoon chemical characteristic listed in the footnotes of Table 1, [AN] of 589 g m^{-3} and pH 8.02 correlate with 0.0023 mol L^{-1} NH_3 (aq) in solution and 1.6×10^{-6} mol L^{-1} NH_3 (g) within the bubbles. This concentration was used to calculate NH_3 bubble emissions in conjunction with the ebullition rate. Similar calculations were made with the Utah data. The model of De Visscher et al. (2002) was used to determine total surface NH_3 gas emissions using average daily windspeed and lagoon chemical parameters. The De Visscher et al. (2002) model was validated using measured NH_3 emissions determined by flux-gradient techniques, with the comparison explaining about 70% of the variability associated with both measurement and model errors (flux measurement error estimated to be ∼15–20%) (Harper, 2005; Harper et al., 2011; Todd et al., 2007). Calculations of the NH_3 emissions from this bubble transfer mass-flux model (Table 1) showed that only 0.03–0.04% of total NH_3 emissions in North Carolina and 0.051–0.052% in Utah were due to this ebullition transport process, and therefore it is not necessary to correct emissions determined by the De Visscher et al. (2002) model for mass-flow NH_3 emissions. Even with NH_3 in the gas bubbles at equilibrium with the liquid phase, the ebullition rate for lagoons would still have to be at least two orders of magnitude larger than any gas bubble emissions measured to date at any time of the year (Harper et al., 2000, 2004, 2014; Weaver

TABLE 1 Determination of NH_3 emissions due to mass flow in gas bubbles that are emitted from the lagoon sediment layer

Lagoon	Time period	Lagoon temp.[a]	Wind speed[b]	Biogas ebullition rate (all gases[c])	Calculated NH_3–N emissions[d]	NH_3–N bubble transport emissions	NH_3 flux bubble transport
		°C	cm s^{-1}	m^3 gas m^{-2} d^{-1}	kg NH_3–N ha^{-1} d^{-1}		% NH_3 emissions
NC-10[e]	7–10 Aug. 1997	29.14	142	0.0221	27.9	0.008	0.030
NC-10	14–15 Aug. 1997	29.97	184	0.0266	30.5	0.010	0.033
NC-10	27–29 Aug. 1997	29.74	244	0.0320	29.7	0.012	0.040
UT-17[f]	Aug. 2004	21.10	305	0.054	60.4	0.052	0.051
UT-18[g]	Aug. 2004	21.06	305	0.052	70.8	0.060	0.051
UT-21[h]	Aug. 2004	20.92	305	0.044	66.0	0.051	0.052

[a] Temperature measured about −3 cm.

[b] From a nearby weather station.

[c] Measured using the technique of Harper et al. (2000).

[d] Based on the model of De Visscher et al. (2002).

[e] Lagoon chemical characteristics: ammoniacal N concentration [AN] = 589 g m^{-3} N; pH 8.02.

[f] Lagoon chemical characteristics: [AN] = 1,500 g m^{-3} N; pH 8.06.

[g] Lagoon chemical characteristics: [AN] = 1,594 g m^{-3} N; pH 8.10.

[h] Lagoon chemical characteristics: [AN] = 1,535 g m^{-3} N; pH 8.02.

et al., 2012) for the bubble NH_3 transport to compare with the diffusive surface transport rates of NH_3 emissions.

3.1 | Ebullition emission enhancement due to turbulence

Ebullition enhancement due to increased surface turbulence has been demonstrated to occur but at ebullition rates much larger than rates commonly observed in manure-processing lagoons. Bubbling rates should be evaluated on a flux per area basis because the enhancement effect is due to turbulence at the surface. Huisman et al. (1990) observed that an ebullition rate of 0.0002 m^3 m^{-2} s^{-1} (17 m^3 m^{-2} d^{-1}) increased mass transfer rates by 25% compared with no bubbling, whereas an ebullition rate of 0.0019 m^3 m^{-2} s^{-1} (160 m^3 m^{-2} d^{-1}) increased mass transfer rates by nearly 500%. Experiments of Monteith et al. (2005) showed 32, 112, and 260% increases in mass transfer over no ebullition for rates of 97, 195, and 292 m^3 m^{-2} d^{-1}, respectively. Although these enhancement effects are large, the ebullition rates of swine lagoons observed in Table 1 would have to be increased 340—5,800 times for similar enhancements to occur in swine lagoons.

Five bubble-enhancement laboratory experiments by Ro et al. (2008) were conducted at lower ebullition rates. In these experiments, the disappearance of aqueous NH_3 was observed over time. Mass transfer coefficients were then calculated from the exponential mathematical fits of the concentration vs. time data for each experiment. The ratio of the mass transfer coefficient for the bubbled experiment compared with the control experiment was used to calculate ebullition enhancement. One experiment (bubble and control) was conducted in a column, and four experiments (each with bubble and control) were conducted in an evaporating pan. In their column experiment, Ro et al. (2008) demonstrated a 75% larger mass transfer coefficient for the bubble solution compared with an identical solution that was not bubbled. They bubbled their column container (0.150 m in diameter, 0.018 m^2) at a rate of 92 cm^3 min^{-1}, which is equivalent to 3.24 m^3 m^{-2} d^{-1} for the column container experiment. This ebullition rate is much larger than the ebullition rates of working lagoons described previously.

When comparing field ebullition measurements with experimental data, it is important to note that ebullition rates change substantially during the year. In order to assess this seasonal variation in ebullition rates, monthly biogas production rate was plotted for three lagoons in Utah (Figure 1). It is clear that wintertime biogas ebullition can drop to ~20% of peak summer emission. The Ro et al. (2008) column ebullition rate is significantly larger than the measured values reported in Table 1 for North Carolina (0.022–0.032 m^3 m^{-2} d^{-1}) and in Figure 1 for Utah (0.01–0.05 m^3 m^{-2} d^{-1}).

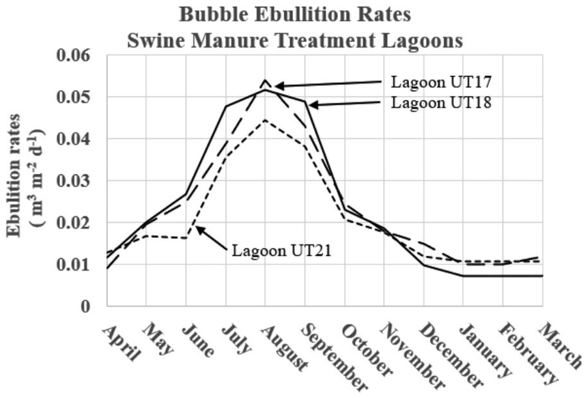

FIGURE 1 Ebullition rates from three production lagoons in the Central Great Basin of Utah

The other four Ro et al. (2008) bubbling experiments were conducted at a bubbling rate (flux per area) that was considerably lower than the column experiment. Although the flux was similar (40–92 cm^3 min^{-1}), the container (evaporation pan) had a much larger surface area (1.2 m in diameter, 0.240 m deep). These bubbling rates correspond to 0.05–0.11 m^3 m^{-2} d^{-1} and are within a factor of two of lagoon ebullition rates reported in Table 1. Concurrent with the much lower bubbling rate, the emission enhancements of 4, 12, 15, and 38% for the four individual 7-h experiments are much lower than seen in the column experiment.

There is strong evidence that the 38% enhancement observed in the pan experiments is an outlier compared with the other three pan experiments. First, the bubbling rate (0.05 m^3 m^{-2} d^{-1}) was different from the other experiments (0.11 m^3 m^{-2} d^{-1}), and no duplicate experiment was conducted. Second, R^2 values for the exponential least squares fit of [NH_3(aq)] vs. time (.75 and .78, bubbled and control, respectively) were lower than the other three experiments (bubbled: .85, .96, .96; control: .89, .93, .96). Third, the rate of disappearance for the control pan was one-third the controls' rates for each of the other three experiments. Finally, it seems unreasonable that an ebullition rate 1.5% of the column experiment (3.24 vs. 0.05 m^3 m^{-2} d^{-1}) would have an enhancement just half of the 75% enhancement of the column experiment. After excluding the outlier, the other three pan experiments in their study demonstrate an ∼10% enhancement, which is less than the experimental error of most models (30% [including model and validation measurement error] in the De Visscher et al. [2002] model).

In experiments by Blanes-Vidal and Nadimi (2011), which were designed to test for increases in NH_3 emissions due to surface disturbances, pre-storage animal wastewater was used without an attempt to replicate lagoon conditions. Although the total ebullition rate was not measured, measured CO_2 baseline emissions were used to estimate a rate of 0.16–0.2 m^3 m^{-2} d^{-1}, assuming 35–45% CO_2. Because these experiments were not designed to measure ebullition enhancement, an ebullition enhancement could not be directly determined. However, the model used to predict the observed CO_2 emissions had a 43% error when "bubble-enhanced" volatilization and surface film formation were neglected. When these two factors were included, the model had an average error of 25%. Thus, these two factors could only account for 18% of the error at an ebullition rate two to four times faster than that observed in working lagoons during maximum production.

3.2 | Predicting ebullition emission enhancement due to turbulence from measured ebullition rates

Although it is possible that ebullition can enhance surface emissions, the question that must be answered is whether ebullition rates for an entire lagoon occur at a rate that emissions have been shown to be enhanced. To answer this question, the average lagoon ebullition rate must be known. Various researchers have measured ebullition rates; these data are summarized in Table 2, arranged according to loading rate of kg volatile solids (VS) m^{-3} d^{-1}. Loading rates can also be represented as m^3 animal $unit^{-1}$ (AU, AU = 450 kg), which can easily be calculated from the number and size of animals and the volume of the lagoon. Using the relationship published in Humenik and Overcash (1976), loading rates in the literature expressed in kg VS m^{-3} d^{-1} were converted to m^3 AU^{-1} and vice versa when only the number of animals and lagoon size were known for easy comparison between studies in Table 2. Although ebullition rates (and corresponding ebullition enhancement) may vary within a lagoon, a single ebullition rate is necessary to predict overall ebullition enhancement. Ebullition rates reported in Table 2 are average ebullition rates unless noted. As Huisman et al. (1990) demonstrated, ebullition enhancement is approximately linearly proportional with ebullition rates; thus, average ebullition enhancement may be estimated from average ebullition rates rather than calculating enhancement for each measurement site and then averaging.

Review of Table 2 shows that the maximum ebullition rates are dependent upon loading rates. With the exception of the Safley and Westerman's (1988) Smith lagoon, all lagoons with a loading rate of less than the recommended loading rate of 0.08 kg VS m^{-3} d^{-1} (ASABE, 2011) have maximum ebullition rates ≤0.10 m^3 m^{-2} d^{-1}. Additionally, the 1986 Unit II lagoon cannot be used to imply average lagoon maximum ebullition rates because the lagoon was dredged prior to the measurements. Safly and Westerman (1988) attributed the abnormally high ebullition rates, compared with the previous year, to fresh animal waste accumulating in the dredged area where the measurement device was located (anchored 11 m from the discharge pipes). Consequently, this measurement

TABLE 2 Lagoon loading rates and ebullition rates

Study	Lagoon ID	Type	Loading rate	Loading rate	Length of study	Number of locations measured	Representative measurement	Average ebullition rate
			kg VS m^{-3} d^{-1}	m^3 AU^{-1}				m^3 m^{-2} d^{-1}
Safley and Westerman (1988)	Unit II (1985)	dairy	0.02	110[a]	34 d (July–Aug.)	4	Semi[b]	0.07
Safley and Westerman (1988)	Butner	poultry	0.02	110 [a]	27 d (June–July)	5	Semi[b]	0.10
Safley and Westerman (1988)	Unit II (1986)	dairy	0.02	110[a]	161 d (June–Sept.)	1	Non[c]	0.35
Harper et al. (2004)	Farrow to Finish	swine	0.022[a]	102	—[d]	—[d]	—[d]	—[d]
Hamilton et al. (2006)	Pilot Scale Bioreactor	swine	0.025	87[a]	6 d (June–Aug.)	1	Semi[e]	0.08 (max)
Weaver et al. (2012)	UT-17	swine	0.026[a]	85	year	6	Representative[f]	0.054 (max), 0.011 (min)
Weaver et al. (2012)	UT-18	swine	0.026[a]	85	year	6	Representative[f]	0.052 (max), 0.11 min
Weaver et al. (2012)	UT-21	swine	0.026[a]	85	year	6	Representative[f]	0.044 (max), 0.009 (min)
Grant et al. (2016)	NC4	swine	0.029[a]	75	—[d]	—[d]	—[d]	—[d]
Harper et al. (2004)	Farrow to Wean	swine	0.029[a]	75	—[d]	—[d]	—[d]	—[d]
Grant et al. (2016)	OK4	swine	0.033[a]	66	—[d]	—[d]	—[d]	—[d]
Grant et al. (2016)	IN4	swine	0.034[a]	64	—[d]	—[d]	—[d]	—[d]
Grant et al. (2016)	OK3	swine	0.036[a]	62	—[d]	—[d]	—[d]	—[d]
Safley and Westerman (1988)	Johnson	swine	0.04	55[a]	54 d (July–Aug.)	5	Semi[b]	0.10

(Continues)

TABLE 2 (Continued)

Study	Lagoon ID	Type	Loading rate	Loading rate	Length of study	Number of locations measured	Representative measurement	Average ebullition rate
Safley and Westerman (1988)	Crantock (1986)	swine	0.04	55[a]	90 d(June–Sept.)	1	Non[g]	0.09
Craggs et al. (2008)	Dairy	dairy	0.046	48[a]	Year	1	Semi[h]	0.032 (yearly average)
Grant et al. (2016)	NC3	swine	0.047[a]	47	—[d]	—[d]	—[d]	—[d]
Safley and Westerman (1988)	UCP Research Station	swine	0.05	44[a]	2 mo (June–Sept.)	4	Semi[b]	0.04
De Sutter and Ham (2005)	Kansas Farm	swine	0.074[a]	30	year	4	Representative[i]	0.025 (yearly average)
Chandler et al. (1983)	Royal Farms	swine	0.11	20 [a]	8 mos (May–Dec.)	1	Semi[j]	0.92 (max), 0.66 (min)
Safley and Westerman (1988)	Smith	poultry digestor	0.16	13.8[a]	20 d (May–June)	5	Semi[b]	0.20
Humeric and Overcash (1976)	Pilot Scale Reactor	swine	0.44	5.0[a]	1	1	NA[k]	0.21
Craggs et al. (2008)	Piggery	swine	0.44	5.0 [a]	year	1	Semi[h]	0.84 (yearly average)

[a] Calculated from equivalent relationship between kg VS m^{-3} d^{-1} and (m^3 AU^{-1}) in Humenik and Overcash (1976).

[b] Each location measured sequentially, all within 15 m of discharge pipes.

[c] Single measurement location within 11 m discharge pipes. Placed over freshly dredged lagoon at a location where fresh waste was collecting.

[d] Ebullition rate not determined.

[e] Emissions measured in 30-min intervals for 12- to 20-h periods.

[f] Measurements were made concurrently at 6 representative lagoon locations.

[g] Single measurement location within 15 m of discharge pipes.

[h] Single location in middle of lagoon.

[i] The lagoon was divided into four zones with a collector in each zone and collectors were randomly moved within one of four sectors within each zone

[j] 1070 m^3 collector (aprox. 1/3 the size of lagoon) was placed in the corner next to the discharge pipe to maximize biogas recovery.

[k] Single experiment. Estimated from the time necessary to collect 0.00095 m^3 biogas.

is clearly unrepresentative of typical lagoon ebullition rates. Additionally, all of the Safley and Westerman (1988) measurements are likely biased high because all measurements were made within 15 m of the discharge pipe and do not represent the entire lagoon. Collecting biogas within 15 m of discharge pipes excludes the majority of a lagoon and leads to nonrepresentative sampling. For example, in the 2-ha lagoon of the study by De Sutter and Ham (2005), collection within 15 m of the discharge pipe would be about 350 m^2 or 2% of the lagoon that is closest to the pipe.

Additional NH_3 emission studies are included in Table 2 to demonstrate that lagoons are commonly loaded below the recommended rate of 0.08 kg VS m^{-3} d^{-1}. Because this a common loading rate, we have chosen to predict ebullition enhancement for lagoons below this recommended loading rate. Ebullition rates with loading rates exceeding this criteria are not discussed further. Review of Table 2 shows that the maximum ebullition rate for a loading rate of 0.08 kg VS m^{-3} d^{-1} is equavlent to 0.1 m^3 m^{-2} d^{-1}. The Ro et al. (2008) experiments predicted a 10% enhancement for a 0.11 m^3 m^{-2} d^{-1} ebullition rate. Thus, the maximum enhancement expected in lagoons in the summertime would be 10%. However, the actual enhancement is probably less. The typical maximum summertime overall lagoon ebullition rates are probably <0.1 m^3 m^{-2} d^{-1}. For example, the ebullition rate of 0.1 m^3 m^{-2} d^{-1} is from a measurement not representative of the entire lagoon (i.e., taken from close to discharge pipe). Our earlier work, not all included in Table 2 (Harper et al., 2000, 2004, 2014; Weaver et al., 2012), represents the measurement of multiple-year studies of 24 lagoons (six gas collectors in each lagoon) with maximum summertime emissions rates <0.055 m^3 m^{-2} d^{-1}. In North Carolina, Harper et al. (2014) found ebullition rates varied between 0.012 and 0.035 m^3 m^{-2} d^{-1}, with a 0.02 m^3 m^{-2} d^{-1} yearly average. In Georgia, the yearly average was 0.023 m^3 m^{-2} d^{-1} (L. A. Harper and R. R. Sharpe, unpublished data, 1994). If we assume the same relationships observed between minimum and maximum ebullition and yearly averages in Utah and Georgia, then the Georgia data would predict a maximum summer ebullition rate of 0.04 m^3 m^{-2} d^{-1}. Additionally, when the dairy and poultry measurements are excluded from Table 2, predicted average maximum ebullition rates are even less. Because more representative ebullition rate measurements are roughly half of the maximum value from Table 2 of 0.1 m^3 m^{-2} d^{-1}, a 5% enhancement is more likely. Whether this maximum enhancement in properly loaded lagoons is 10 or 5%, it only occurs during summer and is much less during cooler months.

If ebullition rates are highest during summer months (Figure 1) and decrease during cooler months, the ebullition enhancement should vary seasonally. A model that neglects this slight enhancement will underestimate emissions in the summer, and this underestimation will decrease in the winter. This hypothesis was tested by comparison with validation measurements for the De Visscher et al. (2002) model, which does not have an ebullition enhancement factor. Review of the De Visscher et al. (2002) method development paper shows the opposite happened as the model slightly overestimated emissions relative to measured emissions in summer.

4 | CONCLUSION

Mass-flow (ebullition or bubble transport) emissions of NH_3 in swine manure treatment lagoons are <0.52% of total measured/calculated lagoon NH_3 emissions. Additionally, biogas ebullition at the rate observed in working lagoons does not significantly (<10%) enhance surface emissions through increased turbulence at the surface. Although ebullition may enhance NH_3 emissions more in overloaded lagoons or in localized areas of lagoons, an overall lagoon NH_3 emission enhancement of >10% is not expected to occur in properly loaded lagoons even in summertime months when ebullition is the largest. Therefore, biogas ebullition, with the ebullition rates described in this paper, need not be accounted for in models designed to calculate NH_3 emissions in swine manure treatment lagoons.

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AUTHOR CONTRIBUTIONS

Kim H. Weaver: Conceptualization; Data curation; Formal analysis; Investigation; Methodology; Resources; Supervision; Writing – original draft; Writing – review & editing. Lowry A. Harper: Conceptualization: Data curation; Formal analysis; Funding acquisition; Methodology; Supervision; Writing – original draft; Writing – review & editing. Alex De Visscher: Conceptualization; Formal analysis; Writing – review & editing. Oswald van Cleemput: Conceptualization; Writing – review & editing.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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APPENDIX

The calculation of the bubble mass transfer coefficient, $k_{\mathrm{L,b,\,NH3}}$ (cm s^{-1}), is taken from Akita and Yoshida (1974):

$$k_{\mathrm{L,b,NH_3}} = 0.5g^{5/8} D_{\mathrm{L,NH_3}}{}^{1/2} \rho_{\mathrm{L}}{}^{3/8} \gamma_{\mathrm{L}}{}^{-3/8} d_{\mathrm{b}}{}^{1/2} \qquad \text{(A1)}$$

where g the acceleration due to gravity (981 cm s^{-2}); $D_{\mathrm{L,\,NH3}}$ is the diffusion coefficient of NH_3 in the liquid phase with a value of 1.84×10^{-5} cm^2 s^{-1}, which was a representative value compiled by Himmelblau (1964) of (1.09–2.23 cm^2 s^{-1}); ρ_{L} is the liquid density (g cm^{-3}); and γ_{L} is the surface tension.

$$\rho_{\mathrm{L}} = 999.85831 + 0.0499881\,T(^{\circ}\mathrm{C}) - 0.007155952T^2\left(^{\circ}\mathrm{C}\right) + 0.000028333T^3(^{\circ}\mathrm{C}) \qquad \text{(A2)}$$

which is accurate to 0.04 kg m^{-3} at 0 to 60 °C.

For ρ_{L} the Equation A2 was used, which was obtained by fitting a polynomial relationship of temperature of the effluent in °C to data of Liley et al. (1984):

The γ_{L} was calculated with Equation A3 recommended by Floriano and Angell (1990):

$$\gamma_{\mathrm{L}} = B\left(\frac{T_{\mathrm{c}} - T}{T_{\mathrm{c}}}\right)^{\mu}\left[1 + b\left(\frac{T_{\mathrm{c}} - T}{T_{\mathrm{c}}}\right)\right] \qquad \text{(A3)}$$

with $B = 0.2358$ N m^{-1}, $T_{\mathrm{c}} = 647.15$K, $\mu = 1.256$, and $b = -0.625$. The accuracy of this equation is about 1% for the range of −27.2 to 60 °C.

The value of $k_{\mathrm{L,b,\,NH3}}$ calculated in Equation A1 refers to bubbles in pure water. In lagoon liquid, the mass transfer is slower due to the presence of solids. This reduction in mass transfer is accounted for multiplying $k_{\mathrm{L,b,\,NH3}}$ by a factor α, which can range from 0.4 to 0.9 depending on the solids concentration in the liquid (Baker et al., 1975; Hwang & Stenstrom, 1985). We used a value of 0.7 in our calculations to determine a value of 0.011 cm s^{-1} for $k_{\mathrm{L,b,\,NH3}}$ in lagoon liquid.

Calculation of rise velocity, u_{b}, and rise time

For the calculation of t used in Equation 9, the rise velocity of the bubbles and the lagoon depth are needed (~3.1 m, a common depth in North Carolina lagoons). For the rise velocity of bubbles in water, the amount of representative data in the literature is limited. Data of O’Brien and Gosline (1935) in a 15-cm-diameter column suggest the relationship between the Reynolds number (Re) and the drag coefficient (C_D) as in Equation A4:

$$C_\mathrm{D} = 0.1725\mathrm{Re}^{0.3} \tag{A4}$$

with $C_\mathrm{D} = 4gd_\mathrm{b}/3{u_\mathrm{b}}^2$ and $\mathrm{Re} = d_\mathrm{b}u_\mathrm{b}\rho_\mathrm{L}/\mu_\mathrm{L}$, where u_b is the bubble rise velocity, and μ_L is the liquid viscosity. The above equation fits the data of O’Brien and Gosline (1935) to within 10%, with Re values ranging from 350 to 10,000, which corresponds to bubble diameters of 2.1–17 mm at 10–30 ˚C. The C_D tended to decrease with increasing column diameter, so the value obtained here is likely an overestimate, leading to an underestimate of the bubble rise velocity, an overestimate of the rise time, and an overestimate of the bubble contamination. The effect of column diameter on C_D values of O’Brien and Gosline (1935) is a factor 2 or less for column diameters ranging from 3 to 15 cm, within the range of Re of interest.

For μ_L (Pa s), the following relationship was used in Equation A5:

$$\mu_\mathrm{L} = 10^{-6}\exp\left(7.38183 - \frac{2,413.769}{T} + \frac{667,268}{T^2}\right) \tag{A5}$$

which is based on data of Lide (1992). Equation A5 is accurate to within 0.5% for pure water. Equation A4 can be rewritten as:

$$u_\mathrm{b} = 2.433g^{1/2.3}{d_\mathrm{b}}^{0.7/2.3}\left(\frac{\mu_\mathrm{L}}{\rho_\mathrm{L}}\right)^{0.3/2.3} \tag{A6}$$

The rise velocity was calculated using Equation A6 to be 0.17 m s^{-1}. Subsequently, the rise time was calculated to be 18 s by dividing the rise depth of the lagoon by the rise velocity.