

Research Article

Effect of ISPAD Anaerobic Digestion on Ammonia Volatilization from Soil Applied Swine Manure

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Received 21 May 2011; Accepted 14 June 2011

Academic Editor: David C. Weindorf

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Swine manure subjected to In-Storage Psychrophilic Anaerobic Digestion (ISPAD) undergoes protein degradation but limited NH_3 volatilization, producing an effluent rich in plant-available N susceptible to more volatilization during land application. This study therefore measured NH_3 volatilization from both ISPAD and open tank (OT) swine manures when applied to 5 different soils (washed sand, Ste Rosalie clay, Upland sandy loam, St Bernard loam and Ormstown silt) within laboratory wind tunnel simulations. After 47 h, the NH_3 volatilized varied with both manure and soil type. For all soils, the ISPAD manure lost less NH_3 compared to OT manure, averaging 46% less. The lower solids content and higher buffering capacity of the ISPAD manure explain the advantage. The Ormstown loam maintained the same NH_3 volatilization rate after 47 h because of higher capillary effect and the St Bernard sandy loam lost the same N mass for both manures, because of a higher pH and buffer pH, with an intermediate CEC resulting in more soil solution NH_3 . Within each manure type, % TAN volatilized was highest for washed sand and lowest for the clay soil. Thus, ISPAD manure can offer up to 21% more plant-available N especially when not soil incorporated following its application.

1. Introduction

In-storage psychrophilic anaerobic digestion (ISPAD) occurs in manure storage tanks with an air-tight cover when its anaerobic microbial community acclimates to ambient conditions [1]. Developed for livestock operations in temperate climatic zones, ISPAD can release 65% of the manure's potential methane while lowering volatile solids by 24% [1]. As opposed to mesophilic, psychrophilic anaerobic digestion limits biogas ammonia (NH_3) levels, despite the breakdown of proteins [2, 3]. However, when land spread, the treated effluent may lose to the atmosphere the conserved total available nitrogen (TAN or NH_4^+ and NH_3), resulting in a net loss of nitrogen lowering its fertilizer value.

Following land spreading, the volatilization of NH_3 -N from swine manure depends on several factors. Some are independent of manure storage and treatment, such as pig diet [4], method of soil application [5], application timing

[6], and subsequent weather conditions [7–9]. Diet manipulations reducing protein intake result in lower manure TAN and less volatilization losses following land application [10]. A data base analysis from field measurements concluded that NH_3 volatilization was proportional to the manure TAN and the percentage released remained constant [7].

The concentration and thus volatilization of NH_3 are also influenced by the manure characteristics and their interaction with the soil properties. The speciation of TAN into NH_3 depends not only on the pH and temperature of the manure [11, 12] but also on the presence of other ionized species [13]. The soil alkalinity and buffering capacity can change the manure pH [11, 14, 15]. The NH_3 speciation equilibrium is further affected by the soil cation exchange capacity (CEC) affecting the level of free NH_4^+ [16]. Furthermore, NH_4^+ can be precipitated by soil solution cations, particularly Ca^{2+} and Mg^{2+} , producing calcite and struvite [12].

Physical aspects of the soil/manure system also intervene. Lower NH_3 volatilization results from higher manure infiltration into the soil, especially when the manure has a low volatile solids content [8]. Nevertheless, manure applied on a dry soil loses its water content releasing NH_3 [17].

Anaerobic digestion can change the physicochemical characteristics of swine manure thereby influencing several of the above-mentioned factors. Untreated and anaerobically digested under mesophilic conditions, swine manure offered the same rate of NH_3 volatilization after application to grassland [18]. In a similar comparison, soil pH and NH_4^+ -N content were found to be more influential following the application of both treated and untreated swine manures to bare soil [19]. In comparison to untreated manure, NH_3 volatilization was 22% less for anaerobically digested manure applied to a bare silty clay loam [20].

While similar nutrient values (N, P, and K) are found for swine manures from all types of operations and in several countries [21–23], plant availability depends on best management practices [24]. Anaerobic digestion degrades organic N releasing TAN [2, 25, 26] readily available for plant uptake. Once soil applied and as compared to untreated manure, digested effluents were found to offer higher plant available nutrients for wheat [27], corn [28], and timothy [29].

Accordingly, ISPAD can enhance the manure N fertilizer value by minimizing biogas NH_3 content as compared to mesophilic systems, while still providing all benefits of anaerobic digestion and higher plant-available N. The objective of the present study was therefore to compare the extent of NH_3 volatilization between ISPAD treated and raw (untreated or open tank) swine manures. This was done by simulating land application of both manures using the wind tunnel technique and monitoring NH_3 release with boric acid traps. Five different experimental soils were used, each offering a similar pH but different cation exchange capacity (CEC), cation saturation level, organic matter content, and water holding capacity.

2. Materials and Methods

2.1. Experimental Manures and Soils. In 2004, a full-scale swine manure ISPAD was established in St. Francois Xavier, Quebec, Canada, using a circular concrete tank, 30 m in diameter and 3.66 m deep, covered with an air-tight membrane (GTI, Fredericton, NB, Canada). The ISPAD was fed swine manure weekly and was emptied in the spring and fall of each year, except for a 0.3–0.6 m depth. In 2010 for the present experiment, manure from this facility was compared to 12-month-old swine manure from the open tank of the Experimental Swine Facility of McGill University at its Macdonald Campus, Montreal, Canada. Produced by hogs fed a standard corn and soybean ration, these two manures were considered comparable in terms of solids and nutrients [21]. All manure samples were collected in March 2010 using a sludge-judge apparatus to obtain a composite sample representing the average of depths and locations within the tanks [1].

Manure samples were analyzed according to standard methods [30] for solids, pH, total Kjeldahl nitrogen (TKN), total ammonia nitrogen (TAN), and phosphorus (P) and potassium (K) content. Total solids (TSs) were determined by drying whole samples at 103°C overnight (VWR, Sheldon Manufacturing, model 1327F, OR, USA). Volatile solids (VS) were determined by incineration of dried samples at 500°C for two hours (*Barnstead Thermodyne*, model 48000, Iowa, USA). Fixed solids (FSs) were computed as the difference between VSs from TS. The pH of all samples was determined using a pH meter (*Corning*, model 450, NY, USA). The TKN, P, and K were determined by digesting samples of each manure with sulphuric acid and 50% hydrogen peroxide at 500°C for 15 minutes (*Hach Canada*, Digesdahl model 23130-20, Mississauga, ON). Subsamples of digestate were used to quantify P and K colorimetrically at a pH of 7, using a spectrophotometer (*Hach*, model DR 5000, Loveland Clo, USA). For TKN, the pH of subsamples was adjusted to 13 using NaOH, and the NH_3 -N content was measured with an NH_3 -sensitive electrode (*Orion*, Boston Mass, USA) connected to a pH meter (*Corning*, model 450, NY, USA). Total ammonia nitrogen was measured in the same way using undigested samples, after adjusting the pH to 13.

The five experimental soils were washed sand (S. Boudrias Inc., Laval, QC, Canada), Ste Rosalie clay from Howick, Canada, 50 km west of Montreal; Upland sandy loam from Ste Anne de Bellevue, Canada at the western tip of the Montreal Island, St Bernard loam also from Ste Anne de Bellevue at the western tip of the Montreal Island, and Ormstown loam from Ormstown, Canada, 70 km west of Montreal. Except for the washed sand, all soils were collected from the ground surface for a minimum organic matter content of 3.9%. All soils were dried and ground before sieving to remove organic particles larger than 6 mm.

All experimental soils were analyzed using standard methods. After soaking for 24 hours in equal amounts of distilled water, pH was determined using a pH electrode [31]. Organic matter content was determined on samples dried at 150°C for 16 hours, using a muffle furnace at 375°C for 16 hours [32]. Minerals and trace elements were measured first by extracting with a Mehlich III solution and then by plasma emission spectrometry [33]. The CEC was determined by saturating the samples with NH_4^+ using an ammonium acetate solution at pH 7 and then quantifying the NH_4^+ released after adding a NaCl solution [34]. Total Kjeldahl nitrogen was measured after sulphuric acid/peroxide digestion using an NH_3 -sensitive probe connected to a pH meter (Orion, Boston, USA). Soil particle size distribution was determined using the hydrometer method [35]. The gravimetric water holding capacity was measured by soaking previously dried subsamples in distilled water for 24 hours and draining under cover to prevent evaporation.

2.2. Experimental Wind Tunnels. Ammonia volatilization tests were conducted using five wind tunnels designed for manure spreading simulations [36]. Measuring 2.0 m in length, with an inlet diffuser and outlet reducer of 0.3 and 0.15 m, respectively, each tunnel sat on a soil pan measuring 1.5 m long \times 0.1 m wide \times 0.05 m deep (Figure 1).

TABLE 1: Characteristics of experimental manures where both the ISPAD or anaerobically digested manure and the open tank or untreated manure are one year old.

Property	Open tank manure	ISPAD manure
TS (gL ⁻¹)	37.7 (1.93)	33.5(4.12)
VS (gL ⁻¹)	27.7 (1.75)	23.0 (3.24)
VS: TS	0.73 (0.01)	0.69 (0.01)
VS: FS	2.8	2.2
pH	7.54 (0.01)	7.60 (0.05)
TAN (gL ⁻¹)	1.31 (0.06)	1.63 (0.08)
TKN (gL ⁻¹)	2.66 (0.20)	2.35 (0.30)
TAN: TKN	0.49 (0.08)	0.69 (0.12)
TKN: FS	2.66	2.33
P (gL ⁻¹)	2.29 (0.49)	2.82 (0.48)
K (gL ⁻¹)	1.42 (0.39)	1.04 (0.16)

The standard deviation is in the parenthesis ($n = 3$). TS: total solids; VS: volatile solids; FS: fixed solids.

similar. The ISPAD manure demonstrated some loss of NH₃ during sampling and transportation, based on its TKN:FS ratio compared to that of the open tank manure.

This combination of similarities and differences provided a wind tunnel comparison based on the significantly different characteristics of the two manures for the 115 kg TKN ha⁻¹ applied. The similar TKN resulted in the same volume of manure being applied, thus conserving similar soil water holding capacity levels. Similar TS but different VS levels were applied. The TAN was the most important difference between manures, which was reported not to affect % N volatilization [7, 19]. Accordingly, the application of ISPAD and open swine manures provided a TAN level of 79 and 56 kg ha⁻¹.

The experimental soils (Table 2) were selected to offer a range of properties, illustrated by the groupings produced by the Student-Newman-Keuls test. Organic matter was similar only between the St Bernard loam and Ste Rosalie clay; gravitational water holding capacity was similar for the Upland sandy loam, St Bernard loam, and Ormstown loam; CEC, particle size distribution, especially clay content, and TKN differed among all soils. The pH was similar between the St Bernard loam and Ste Rosalie clay at 6.9 and 6.8, respectively, but different for the rest of the soils offering a pH of 6.3 to 6.5. The mass balance attempted between the initial soil and final soil manure TKN levels were inconclusive because the applied manure TKN was much smaller.

3.2. Ammonia Volatilization. The NH₃ volatilized from all five soils and the two experimental swine manures are compared in Figures 2(a) and 2(b). After 47 hours, the ISPAD swine manure had lost significantly less TAN, from 8 to 37% of that applied, while the open tank manure had lost from 25 to 61%. Accordingly, the ISPAD manure suffered from 75 to 50% less TAN losses as compared to the open tank manure, depending on the soil type. Considering that the two experimental manures offered similar properties except for their treatment, reflecting VS:TS and TAN:TKN ratio,

anaerobic digestion was found to reduce NH₃ volatilization. Similar results were obtained in a field experiment using different crops grown on a loamy soil in Germany [38]. As compared to untreated manure, anaerobically digested manure lost volatilized NH₃ equivalent to 14.2 as opposed to 13% of its total N applied, which represents 20 as opposed to 26% of its TAN.

The ISPAD manure not only suffered significantly less NH₃ volatilization losses over 47 hours but also exhibited a rate of loss which leveled off at 47 hours as opposed to that of the open tank manure. After 47 hours, the ISPAD manure was losing TAN at a rate of 0.25 to 0.05% h⁻¹ for all five experimental soils, as compared to the open tank manure losing TAN at a rate of 1.7 to 0.25% h⁻¹.

The statistical analysis using both mg NH₃-N and % TAN volatilized revealed that the effect of both manure and soil types was significant ($P < 0.003$ for mg N and $P < 0.0001$ for % TAN), with no significant interaction between the factors in either case. The significance of manure effect in mg N confirms that the results were not limited by air saturation in NH₃ inside the wind tunnels, which would have resulted in equal values among tunnels despite higher % TAN losses. Therefore, the remaining results will be presented in terms of % TAN volatilized.

Past research demonstrated a consistent % TAN volatilized for different application rates, with other factors held constant. For the present study, the significant effect results from the manure treatment as both manures exhibited similar properties. For anaerobically digested manure, the specific properties reducing NH₃ volatilization are lower volatile solids allowing for an improved infiltration into the soil and more complex ionic solution lowering TAN speciation into NH₃ [8, 13].

Comparing soil type, the % TAN volatilized results were grouped using the Student-Newman-Keuls method, indicating that, for each manure type, volatilizations from the Upland sandy loam, St Bernard loam, and Ormstown loam soil series were statistically similar while those from the Ste Rosalie clay and the washed sand were each significantly different. For each manure type, volatilization was highest for the washed sand, intermediate for the three similar soils, and lowest for the Ste Rosalie clay, the same grouping observed for H₂O holding capacity and CEC.

Exploratory plots of % TAN volatilized versus each individual soil property also revealed patterns suggesting linear relationships for water holding capacity, CEC and cation saturation. These relationships were examined using a two-factorial rather than a blocked experimental design, which compared the qualitative rather than quantitative soil type values. A variety of combinations revealed a significant effect of the water holding capacity and CEC ($P < 0.0001$), but only when considered separately. The use of only two manure types limited the scope of analysis available, but interesting leads for future research suggest extracting a numerical equation relating the appropriate manure and soil characteristics to % TAN volatilized.

Table 3 summarizes the % and mass (kg ha⁻¹) TAN volatilized in 47 h for each manure-soil combination. The ISPAD manure was found to lose 46% less TAN than the

TABLE 2: Characteristics of the five experimental soils used to measure NH₃ volatilization for the two experimental manures, untreated (open tank) and anaerobically treated (ISPAD).

Property	Washed sand	Ste Rosalie clay	Upland sandy loam	St Bernard loam	Ormstown loam
Organic matter (%)	0.1 (0.0)	6.2 (0.5)	5.0 (0.3)	6.5 (0.4)	3.9 (0.2)
H ₂ O capacity (%)	14.3 (0.0)	32.8 (1.6)	24.8 (1.7)	25.4 (1.5)	23.8 (2.5)
Particle size (%):					
Sand	82.9 (0.9)	7.4 (1.7)	71.2 (1.8)	38.6 (1.5)	1.6 (3.4)
Silt	0.5 (0.9)	25.7 (1.5)	6.8 (1.7)	31.3 (1.9)	62.2 (1.3)
Clay	16.6 (0.9)	66.9 (2.2)	22.0 (0.1)	30.1 (0.4)	36.3 (2.2)
pH	6.3 (0.1)	6.8 (0.1)	6.5 (0.1)	6.9 (0.3)	6.5 (0.9)
Buffer pH	7.3 (0.1)	7.2 (0.1)	6.9 (0.1)	7.3 (0.3)	7.1 (0.4)
CEC (cmol kg ⁻¹)	2.0 (0.5)	36.8 (2.8)	18.3 (1.0)	23.3 (2.2)	20.6 (1.1)
Cation saturation (%)	26.0 (5.9)	92.0 (2.6)	73.0 (3.5)	90.6 (8.8)	81.8 (17.3)
TKN (g kg ⁻¹)	2.4 (0.6)	5.4 (0.8)	4.4 (0.2)	3.5 (0.9)	3.7 (1.3)
TAN (mg kg ⁻¹)	3.0 (2.0)	3.0 (0.4)	6.0 (1.0)	5.0 (3.0)	8.0 (3.0)

The standard deviation is presented in the parenthesis ($n = 3$).

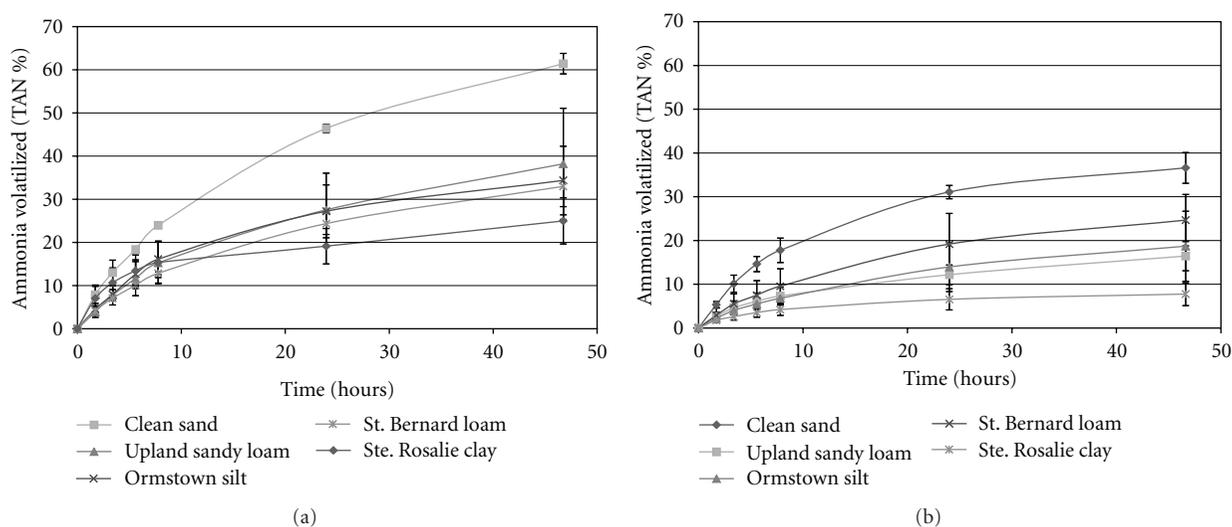


FIGURE 2: Cumulative NH₃ volatilized during 47 hours following the land application of untreated swine manure from the open tank (a) and anaerobically treated swine manure ISPAD (b). The NH₃ volatilization was measured using the laboratory wind tunnels. The data points are the average of $n = 3$ and the error bars represent \pm one standard deviation.

TABLE 3: Fraction of the manure TAN volatilized in 47 hours of wind tunnel simulations for the five experimental soils and two manures, untreated (open tank) and anaerobically digested (ISPAD).

Soil type	Open tank manure		ISPAD manure		Average	
	% manure	kg ha ⁻¹	% manure	kg ha ⁻¹	%	kg ha ⁻¹
Washed sand	61.4 (2.4)	34 (1.3)	36.6 (3.5)	29 (2.8)	49.6	31.5
Upland Sandy Loam	38.2 (12.9)	21 (7.1)	16.4 (3.3)	13 (2.6)	27.3	17.0
Ormstown Loam	34.3 (7.9)	19 (4.4)	18.7 (8.0)	15 (6.4)	26.5	17.0
St Bernard Loam	33.0 (4.7)	19 (2.7)	24.7 (5.9)	20 (4.8)	28.8	19.5
Ste Rosalie Clay	25.0 (5.4)	14 (3.0)	7.8 (2.6)	6 (2.1)	16.4	10
Average	38.6	21.4	20.8	16.6		

The standard deviation is presented in the parenthesis ($n = 3$).

The % value indicated the percentage of the TAN in the applied manure while the kg ha⁻¹ value indicates the mass volatilized.

TABLE 4: Manure N fertilizer value for similar P and K applications for the two experimental manures, untreated (open tank) and anaerobically digested (ISPAD).

	Open tank manure	ISPAD manure
Case 1: Ideal, $N_{\text{available}}$ (gL^{-1})	1.78	1.88
Case 2: Average, $N_{\text{available}}$ (gL^{-1})	1.25	1.48
Case 3: Uncontrolled, $N_{\text{available}}$ (gL^{-1})	0.80	0.97

Case 1 refers to immediate soil incorporation for a spring application, Case 2 refers to soil incorporation after 48 hours for a summer application, and Case 3 refers to leaving the manure at the soil surface for a fall application.

open tank manure. The washed sand lost the most % TAN while the Ste Rosalie clay lost the least at 33% less than the washed sand. The 3 intermediate soils lost approximately 54% of the TAN compared to the washed sand. Interestingly enough, the St Bernard loam lost the same mass of $\text{NH}_3\text{-N}$ for both manure types, likely because of its higher pH and buffer as compared to the other soils and average CEC, resulting in more soil solution NH_3 . Accordingly, the ISPAD manure benefited from the combined effect of its lower volatile solids (VSs) and a more complex ionic solution lowering TAN speciation into NH_3 resulting in lower volatilization for higher levels of plant-available nitrogen [39].

3.3. ISPAD Manure N Fertilizer Value. Because of stringent requirements for nutrient management planning all over North America, the Quebec Ministry of Environment has produced detailed methods for calculating the fertilizer value of manures [34, 40]:

$$N_{\text{available}} = \left(\text{TAN} + \left(N_{\text{organic}} \times \text{CEFO} \right) \right) \times \text{CV}^{-1} \times \text{CA}^{-1} \times \text{CP}, \quad (1)$$

$$N_{\text{organic}} = \text{TKN} - \text{TAN},$$

where CEFO is the organic fraction efficiency factor based on C:N ratio, CV is the volatilization factor based on land application method, CA is the availability factor based on application date (spring or fall), and CP is the previous application factor based on years of manure applied.

Using (1), $N_{\text{available}}$ was calculated for the two experimental manures, assuming three possible cases selected to illustrate a full range of situations: Case 1 pertained to an immediate incorporation of the manure into a clay soil supporting row crops, in the spring; Case 2 pertained to the incorporation within 48 hours of the manure into a sandy loam soil in row crops, during the early summer; Case 3 pertained to manure left at the surface of a sandy loam soil supporting a hayfield, in the autumn. In all cases and for simplicity, no manure was presumed previously applied to the fields, thus $\text{CP} = 1$. For both manures, a C:N ratio in the range of 6 to 10:1 was assumed, based on the VS and TKN values (Table 1). The CV value for the ISPAD manure was modified using the ratio of 0.53 obtained by comparing NH_3 volatilized between the ISPAD and open tank manures in Table 3:

$$\text{CV}_{\text{ISPAD}} = 1 + ((\text{CV} - 1) \times 0.53). \quad (2)$$

The resulting N fertilizer values summarized in Table 4 demonstrate that in Case 1, representing the ideal manure land-application conditions, the ISPAD manure has a modest advantage of 6% over the open tank manure. This advantage increases to 18% under Case 2 where manure is spread on land and then incorporated within 48 hours. For Case 3, where no soil incorporation is practiced, the ISPAD manure offers the highest advantage of 21%. Accordingly, for the same P content, ISPAD manure can provide up to 21% more plant-available N than open tank manure, thus reducing the mineral nitrogen required for top-up by an equivalent amount.

4. Conclusions

The objective of this study was to compare the NH_3 volatilization potential of swine manure treated by a five-year-old in-storage psychrophilic anaerobic digestion system (ISPAD) against that from an open tank. The study simulated field spreading in the laboratory using wind tunnels and five soils offering a different texture and chemical properties.

The study revealed the following.

- (i) For all experimental soils, the % TAN volatilized from the ISPAD manure was on the average 46% lower than that from an open tank indicating the beneficial effect of anaerobic digestion, such as lowering the volatile solids reflecting the suspended solids concentration, to improve infiltration and producing a more complex ionic solution lowering TAN speciation into NH_3 .
- (ii) Water holding capacity and cation exchange capacity were the most important soil parameters influencing NH_3 volatilization.
- (iii) The ISPAD and open tank manures offered a TAN : TKN ratio of 69 and 49%, respectively; coupled with a lower NH_3 volatilization, ISPAD manure can thus increase by up to 21% the plant-available N for the same P and K value, as compared to open tank manure.

Further research is required to identify more clearly the parameters of ISPAD manure which facilitate its lower NH_3 volatilization during land spreading.

Acknowledgments

The authors wish to acknowledge the financial contributions of the Natural Science and Engineering Research Council of Canada, Geomembrane Technologies Inc., of Fredericton NB, Canada, and the Coop Fédérée (Montréal, Canada), the technical contribution of Consumaj Inc., of Ste-Hyacinthe, QC, Canada, and the personal contributions of Dr. Alice Cherestes.

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