RECOVERY OF AMMONIA FROM POULTRY LITTER USING GAS-PERMEABLE MEMBRANES

M. J. Rothrock Jr., A. A. Szögi, M. B. Vanotti

ABSTRACT. *The removal and recovery of gaseous ammonia from poultry litter can benefit bird health and productivity and reduce environmental concerns of emissions from poultry production. We investigated the potential use of gas-permeable membranes as components of a new process to capture and recover ammonia in poultry houses. This process includes the passage of gaseous ammonia through a microporous hydrophobic membrane, capture with a circulating diluted acid on the other side of the membrane, and production of a concentrated ammonium salt. In bench-scale prototype testing using tubular expanded polytetrafluoroethylene (ePTFE) membranes and a 1 N acidic solution (sulfuric acid), the technology captured and recovered 96% of the ammonia lost from poultry litter. The recovery of ammonia could mimic the slow release during flock production or could be accelerated to a few days using hydrated lime amendments. The membrane manifolds can be placed close to the litter surface (above or below), reducing the exposure of the birds to ammonia. Considering that the ammonia is captured inside the houses, this technology could help reduce ventilation and energy needs to lower ammonia levels in poultry houses. The results obtained in this study show that the use of gas-permeable membrane technology could be an effective approach to recover ammonia from poultry litter. The final products are (1) cleaner air inside the poultry houses with benefits to bird health and reduced environmental emissions, and (2) a concentrated liquid nitrogen that can be re-used in agriculture as a valued fertilizer.*

Keywords. *Ammonia capture, Ammonia recovery, Animal waste treatment, CAFOs, Poultry litter.*

One of the largest environmental concerns associated with confined poultry production is the loss of ammonia gas (NH_3) from manure. Volatilization of NH_3 inside poultry housing often results in an excessive accumulation of NH_3 in the air, which can negatively affect the health of both workers and birds (Kirychuk et al., 2006; Rylander and Carvalheiro, 2006). Numerous studies have shown the detrimental effect of high levels of NH_3 on bird productivity (Dawkins et al., 2004; Ritz et al., 2004; Yahav, 2004). Although increased ventilation can lower the NH_3 in poultry houses to safe levels, it is expensive due to energy costs during winter months (Moore et al., 1995). Since NH_3 cannot be effectively contained within the house structure, NH_3 emissions may contribute to air pollution, atmospheric deposition, and health concerns for nearby residents (Edwards and Daniel, 1992; Wheeler et al., 2006; Wing and Wolf, 2000). Conservation and recovery of nitrogen (N) is also important in agriculture because of the high cost of commercial NH_3 fertilizers. Thus, there is major interest among producers and the public in implementing best control technologies that would abate NH_3 emissions from confined poultry operations by capturing and recovering N.

Abatement technologies to reduce NH_3 from poultry houses can be classified into four broad categories based on their mode of action. The first and most widely used technology is to keep NH_3 levels down inside the poultry houses by increasing ventilation. The second technology adds to the previous method by treating the NH_3 in the exhaust air from the houses using scrubbing or filtration techniques, thus preventing its release into the environment. These techniques consist of removal of NH_3 from livestock houses by forcing the house air through an NH_3 trap, such as an acidic solution (scrubbers), or through a porous filter with nitrifying biofilms that oxidize NH_3 to nitrate (biotrickling or organic filters) (Melse and Ogink, 2005; Pagans et al., 2005). The third technology is to selectively pull and treat the air near the litter surface, where NH_3 levels are more concentrated, using dedicated ventilation systems independent of the house ventilation system (Lahav et al., 2008). The fourth approach is the use of chemical amendments mixed directly into the poultry litter to prevent NH_3 volatilization, without the need of additional ventilation to move NH_3. These amendments act by either inhibiting microbial transformation of urea or uric acid into NH_3 or by acidification and subsequent conversion of volatile NH_3 to non-volatile ammonium (NH_4^+). Several chemical amendments have been widely used for their ability to control or reduce NH_3 release from poultry litter and manure, such as $Al_2(SO_4)_3 \cdot 14\ H_2O$ (Al+Clear, General Chemical, Parsippany N.J.), $NaHSO_4$ (PLT, Jones-Hamilton Co., Walbridge, Ohio), and acidified clays (Poultry Guard, Wynco

---

Submitted for review in September 2009 as manuscript number SE 8205; approved for publication by the Structures & Environment Division of ASABE in July 2010.

The authors are **Michael James Rothrock Jr.,** Microbiologist, **Ariel A. Szögi, ASABE Member,** Soil Scientist, and **Matias B. Vanotti, ASABE Member Engineer,** Soil Scientist, USDA-ARS Coastal Plains Soil, Water, and Plant Research Center, Florence, South Carolina. **Corresponding author:** Michael James Rothrock Jr., USDA-ARS New England Plant, Soil, Water Laboratory, Portage Rd., University of Maine, Orono, ME 04469; phone: 207-581-3304; fax: 207-866-0464; email: michael.rothrock@ars.usda.gov.

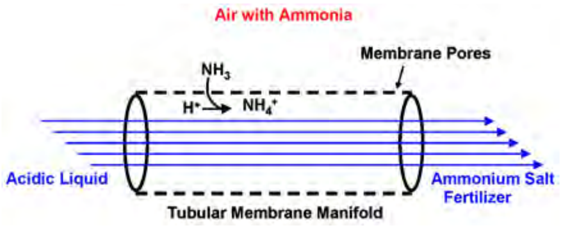

Figure 1. Cross-sectional diagram of ammonia capture using hydrophobic gas-permeable tubing. Ammonia gas (NH_3) permeates through hydrophobic membrane walls with micron-sized pores, where it combines with the free protons (H^+) in the acid solution to form non-volatile ammonium ions (NH_4^+).

Distributors, LLC, Fruitland, Md.) (Cook et al., 2008; Moore et al., 2000; Moore et al., 1995; Rothrock et al., 2008). Although N is conserved unvolatilized in the poultry litter, NH_3 is not recovered as a separate product as with the scrubbing techniques. Recovery of NH_3 is a desirable feature because it can be exported off the farm, solving problems of N surpluses in concentrated poultry production regions.

A novel approach to NH_3 removal from poultry houses was investigated in this study that combines some of the advantages and benefits mentioned above using passive gas-permeable membranes that are placed inside the poultry house near the NH_3 source (Szögi et al., 2010). Hydrophobic gas-permeable membranes can be made of polypropylene (Shindo et al., 1981), polyethylene/polyurethane composites (Lee and Rittmann, 2000), or polytetrafluoroethylene (PTFE) (Blet et al., 1989). This new technology recovers N in a concentrated purified form but is not dependent on intense air movement. This concept includes the passage of gaseous NH_3 through microporous hydrophobic gas-permeable membranes and its capture in a circulated acidic solution with concomitant production of a concentrated ammonium salt. Once NH_3 is in contact with the acidic solution, it reacts with free protons (H^+) to form non-volatile ammonium (NH_4^+) salt, which is retained and concentrated in the acidic solution (fig. 1).

Objective

The objective of this study was to test the technical feasibility of using gas-permeable membranes as a new approach to remove and recover NH_3 from poultry litter. To achieve this, laboratory-scale chambers using a circulated acidic solution contained within a tubular ePTFE membrane were constructed, and the ability of this system to recover and concentrate N from poultry litter was tested under normal and enhanced NH_3 volatilization conditions.

Materials and Methods

Process Configuration

The basic process configuration used in all experiments in this study is shown in figure 2. An acidic solution contained in an acid tank was continuously recirculated into the chamber containing the poultry litter. Once inside the chamber, the acid was contained inside a tubular gas-permeable membrane, allowing for the passage of NH_3 gas emitted by the litter and subsequent recovery and concentration of the N as an ammonium salt.

A picture of one of the chambers used in this study is shown in figure 3. The chamber consisted of a 2 L, polyethylene terephthalate (PET), wide-mouth jar, 18 cm (h) × 12 cm (dia.), with a threaded polyethylene lid (Cole-Parmer, Vernon Hills, Ill.). There were a total of five ports in the lid of the chamber, two for acid inflow-outflow, one for venting air (through tubing with glass wool) to ensure ambient pressure and aerobic conditions inside the chamber, and the remaining two ports allowed headspace air sampling. Tygon tubing (4.75 mm I.D, 6.35 mm O.D., 0.8 mm wall; Cole-Parmer) was used for the inflow and outflow lines outside of the chamber. The chamber contained 300 g of poultry litter with a height inside the chamber of about 5 cm. The acid tank (fig. 2) consisted of a 500 mL glass flask containing 300 mL 1 N H_2SO_4. A peristaltic Manostat pump (Cole-Parmer) was used to continuously circulate the acid through the tubular membranes inside the chamber and back into the acid tank using flow rates of 70 to 80 mL d^{-1}. The flow rate was selected from a previous laboratory experiment that indicated that low (70 to 80 mL d^{-1}) or high (240 to 320 mL d^{-1}) flow rates of the acidic solution through the membrane system did not significantly affect NH_3 recovery (data not shown). Therefore, the lower flow rate was used to prolong the life of the pump tubing.

Gas-Permeable Tubing

Gas-permeable tubing made of expanded polytetra-fluoroethylene (ePTFE) (Phillips Scientific, Inc., Rock Hill,

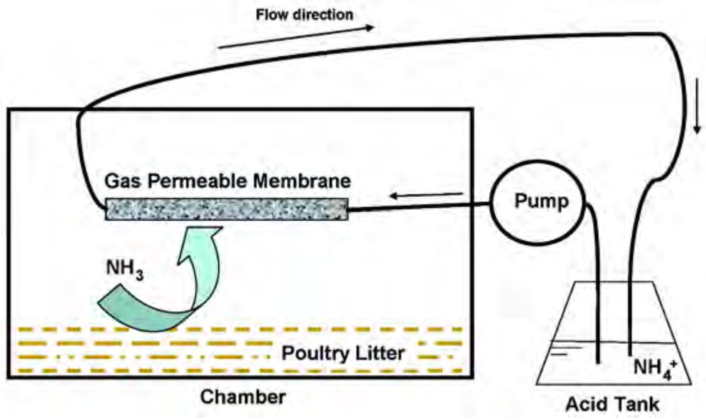

Figure 2. Diagram of the basic process configuration for NH_3 recovery using the gas-permeable membranes.

Figure 3. Chamber used in this study to determine the feasibility of using ePTFE gas-permeable membrane system to capture and recover NH_3 from poultry litter.

S.C.) was used in the interior of the chamber for NH_3 capture. The length of the tubing used in all experiments was 66 cm. Three types of ePTFE tubing were used in this study. The characteristics and scanning electron micrographs of each of the three types of ePTFE tubing are shown in table 1 and figure 4, respectively.

POULTRY LITTER CHARACTERISTICS

The bedding material that constituted the base of the broiler litter in all experiments was wood chips. Broiler litter used for the experiments was collected from a 25,000-bird broiler house in Lee County, South Carolina. At the time of sampling, the house was empty and between the second and third flock (five flocks per year). Two large composite litter samples were taken in two transects along the house, in its center section (between water lines), and placed in 160 L containers. The containers were sealed and transported to the laboratory. A 15 kg portion of the litter was passed through a 5.8 mm sieve and placed in cold storage (-65°C) prior to laboratory experiments. The properties of the poultry litter are listed in table 2.

Table 1. Physical characteristics of the different ePTFE tubular membranes used in this study.

Type	Inner Diameter (mm)	Wall Thickness (mm)	Pore Size (µm)	Bubble Point (kPa)
A	4.00	0.25	1.75	34.5
B	5.25	1.00	5.75	241.3
C	8.75	0.75	2.50	206.8

Table 2. Poultry litter properties.

Parameter	Unit	Value[a]
Moisture content[b]	%	19.7
Volatile solids[c]	%	78.6
pH	--	9.06
Total N[d]	g kg^{-1}	26.3
NH_4-N[d]	g kg^{-1}	13.7
Total C[d]	g kg^{-1}	352
Bulk density	g mL^{-1}	0.3864

[a] Values are means of triplicate litter samples (*n* = 3).
[b] Percent of total mass as measured after drying for 24 h at 105°C.
[c] Percent of total solids as measured after ashing at 550°C for 30 min.
[d] Dry weight basis.

LABORATORY EXPERIMENTS

Four experiments were performed to test the feasibility of using ePTFE tubular membranes in conjunction with an acidic solution to capture and recover NH_3 volatilized from poultry litter. The first experiment determined the general application using three different ePTFE membranes. The second experiment determined if NH_3 recovery could be enhanced with different placements of the membranes with respect to the litter surface. The third experiment determined the maximum capture capacity of the membranes by addition of urea to the poultry litter. The fourth experiment evaluated if the release of NH_3 from the litter could be recovered quickly through the use of hydrated lime treatments in combination with the use of membrane technology.

All four experiments included two replicates for all treatments and controls. In all experiments, 300 mL of 1 N H_2SO_4 was circulated at a flow rate of 70 to 80 mL d^{-1} for a total time of 21 days. The acid solution was sampled daily, and the headspace air was sampled weekly. The pH of the acidic solution was monitored using pHydrion Insta-Chek 0-13 litmus paper (Micro Essential Laboratory, Brooklyn, N.Y.). For the air sampling, 15 to 20 volumes of headspace air was evacuated at a rate of 1500 to 2000 mL min^{-1} for 10 to 15 min from the chamber. The NH_3 from the headspace air

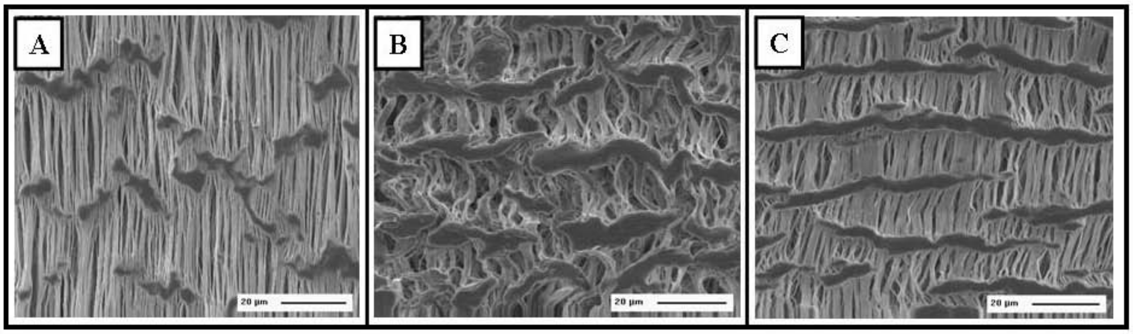

Figure 4. Scanning electron micrograph images for the three different ePTFE tubular membranes used in this study showing different pore structures. All images were taken at 1000× magnification, and the scale bar is equivalent to 20 µm in length. All three tubular membranes were used for the first experiment, while only ePTFE Type B (image B) was used for subsequent experiments.

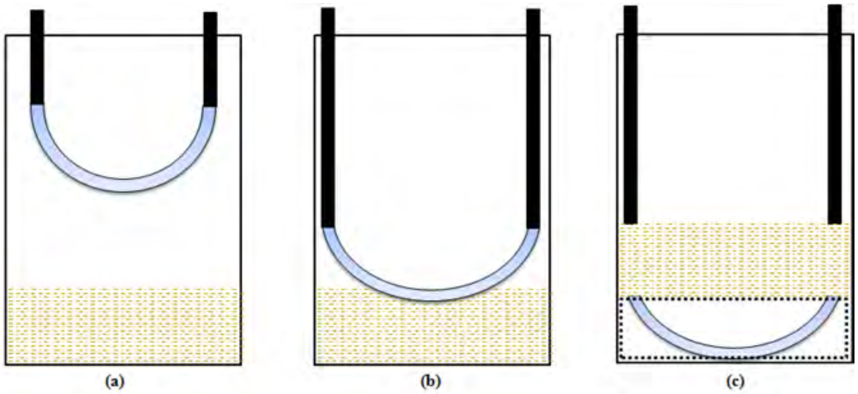

Figure 5. Positioning of the ePTFE tubular membrane (a) above, (b) on, and (c) under the litter surface. The black tubing represents the impermeable Tygon tubing, and the light-colored tubing represents the gas-permeable ePTFE tubing. The dashed box surrounding the ePTFE tubing in (c) represents the nylon mesh pocket that supported the ePTFE tubing under the litter.

was trapped in 1 N H_2SO_4 via glass impingers according to Poach et al. (2004). A sample of 0.3 mL of the 1 N H_2SO_4 solution in the glass impinger was used for the determination of NH_3 headspace concentration. After headspace evacuation, the lid of the chamber was removed, the litter was mixed by hand, and a representative grab sample (12 to 15 g) was taken prior to resealing the lid. Liquid acid samples from the acid tank and impingers (0.3 mL) were diluted into 2.7 mL ultra-pure water, capped, and stored at 4°C, and litter samples were stored at -20°C until analysis. Duplicate control chambers were set up containing litter but no ePTFE tubing and sampled weekly to determine headspace NH_3 and litter characteristics without an NH_3 removal system. In addition, a 500 mL Erlenmeyer flask was set up as an acid tank control (not connected to any chamber) that was sampled at the same time as the other acid solution samples. The starting weight of poultry litter was 300 g for each chamber, and all experiments were performed at ambient pressure and temperature room conditions.

Experiment 1: General Feasibility of Gas-Permeable Membranes to Recover Ammonia from Poultry Litter

The first experiment was designed to determine the general feasibility of using ePTFE tubular membranes in the recovery of NH_3 released from poultry litter. Three different types of ePTFE tubing, designated here as types A, B, C, were tested (table 1 and fig. 4). The membrane tubing inside the chamber had the same length (66 cm) but varied in terms of wall thickness, pore size, and bubble points. Placement of the ePTFE tubing in this experiment was 5 cm above the litter surface (as shown in fig. 5a).

Experiment 2: Effect of Membrane Position on Ammonia Recovery

The second experiment was designed to determine if placement of the ePTFE tubing with respect to the litter surface had an effect on NH_3 recovery. Type B ePTFE tubing (table 1) was used for this experiment. The tubing was placed inside the chamber in the following three positions (fig. 5): (a) 5 cm above the litter surface, (b) directly on the litter surface, and (c) below the litter and inside a pocket made of 300 μm nylon mesh (Krystal Klear Filtration, Winamac, Ind.) to support the tubing under the weight of the litter.

Experiment 3: Removal Capacity under Enhanced Ammonia Volatilization Conditions

The third experiment tested the capacity of the membranes to trap NH_3 by enhancing the release of NH_3. To achieve this, organic nitrogen (10 g of urea containing 4.6 g of N) was added to a chamber containing litter at the beginning of the experiment, resulting in a urea concentration of 5% (w/w). This accounts for about twice the normal input of N for an entire grow-out in an average house (Naber and Bermudez, 1990). The added urea acted as a substrate to enhance NH_3 production and volatilization from the litter. For comparison, a chamber with litter and 0% urea addition was used as a control treatment.

Experiment 4: Accelerated Recovery of Ammonia with Membrane Technology

The goal of the fourth experiment was to determine if NH_3 could be recovered quickly from the litter through the use of chemical treatment in combination with the use of membrane technology. To achieve this, amendments were added to the litter to chemically enhance NH_3 production and volatilization through the addition of hydrated lime [$Ca(OH)_2$] at four applications rates of 0%, 0.4%, 2.0%, 4% w/v (0%, 1%, 5%, and 10% w/w). Hydrated lime was mixed with the litter by vigorous shaking in a plastic bag and immediately placed in the chamber. Hydrated lime raised the pH of the litter ($\geq$10 units) to convert available non-volatile NH_4-N to volatile NH_3-N. Hydrated lime has been historically used for disinfection and NH_3 management of poultry litter (Shah et al., 2006; Yushok and Bear, 1948).

ANALYTICAL METHODS

All liquid samples were analyzed for NH_4-N according to Standard Method 4500-NH_3 G (APHA, 1998). Total Kjeldahl N (TKN) in solid samples was determined in digestion extracts using H_2SO_4 (Pote and Daniel, 2000). The NH_4-N and NO_3-N were extracted from the litter using a 60:1 2 M KCl:litter mixture that was shaken (200 rpm) for 30 min followed by gravity filtration through Whatman filter paper, size 42 (Whatman International, Ltd., Maidstone, U.K.) (Peters et al., 2003). All NH_4-N, NO_3-N, and TKN analyses in solid samples were determined by colorimetry using an AutoAnalyzer II (Technicon Instruments Corp., Tarrytown, N.Y.). Elemental analysis for total C and N was done by dry combustion (Leco Corp., St. Joseph, Mich.). All litter analyses were reported on a dry weight basis. Moisture content of the poultry litter was determined by oven drying the litter at 105°C to constant weight. The dried sample was ignited in a muffle furnace at 550°C for 30 min to determine volatile solids (VS). Litter pH was measured electrometrically using a combination pH electrode at a 5:1 deionized water:litter ratio. Data were statistically analyzed by means and standard errors (proc MEANS), linear regression (proc REG), analysis of variance (proc ANOVA), and least significant difference at a 0.05 probability level ($LSD_{0.05}$) for multiple comparisons among means with SAS (version 9.2, SAS Institute, Inc., Cary, N.C.).

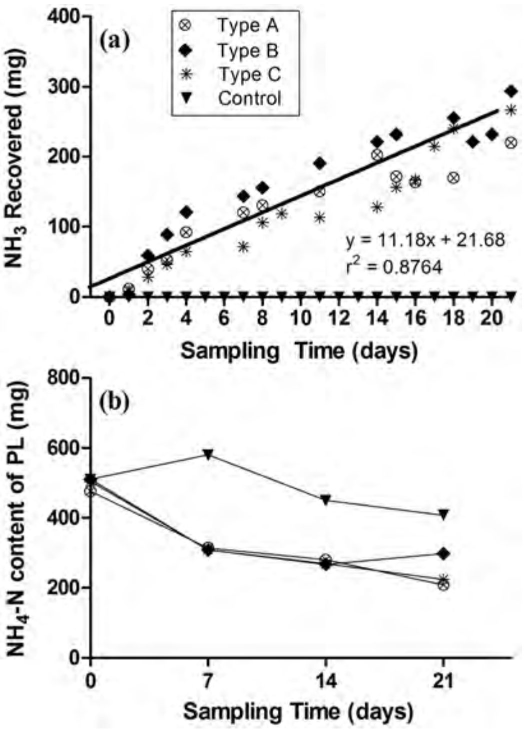

Figure 6. Mass of (a) NH_3 recovered in the acidic solution and (b) NH_4-N remaining in the poultry litter (PL) from chambers possessing three different types of ePTFE tubular membranes. The controls were run for both the acidic solution and the poultry litter: (a) acid without poultry litter, and (b) chamber without ePTFE NH_3 capture. All data points are means of duplicate chambers.

RESULTS AND DISCUSSION

EXPERIMENT 1: GENERAL FEASIBILITY OF GAS-PERMEABLE MEMBRANES TO RECOVER AMMONIA FROM POULTRY LITTER

The membrane system recovered about 96% of the NH_3 lost from the litter during the 21-day evaluation (fig. 6, table 3). Figure 6a shows a steady linear ($y = 11.18x + 21.68$, $r^2 = 0.8764$) increase in NH_3 accumulation in the acidic solution during the study as NH_3 was slowly released from the litter, as compared to the control where no NH_3 accumulated in the acidic solution. The three evaluated membranes performed similarly, with no significant difference in the total mass of NH_4-N accumulated in the acidic solution by the end of the experiment (table 3). On the average, the total NH_3 recovered in the acidic solution was 267.0 mg, compared to 278.4 mg lost from the litter during the same period, resulting in a 96% mass recovery. The NH_3 capture rate, on a surface area basis, was 1.37, 1.29, and 0.70 g m^{-2} d^{-1} for types A, B, and C, respectively. As the NH_3 was being recovered from the air with the membranes, the NH_4-N contained in the litter decreased accordingly; on the other hand, the NH_4-N content in the control treatment changed little (20%) throughout the experiment (fig. 6b). This suggests that the removal of NH_3 from the chamber using membranes allowed for a change in the equilibrium concentration of ammoniacal-N in the litter. The high removal efficiencies obtained in this experiment showed that the concept of using NH_3 gas-permeable membranes for poultry litter applications is technically feasible.

EXPERIMENT 2: EFFECT OF MEMBRANE POSITION ON AMMONIA RECOVERY

The relative position of the tubular membranes (above, on, or under the litter) did not significantly affect the total mass of NH_3 recovered by the system (fig. 7a; p = 0.4776) nor the mass of the NH_4-N remaining in the litter after volatilization (fig. 7b; p = 0.7908). Therefore, the results from the three treatments were pooled together to perform a weekly mass balance of the NH_4-N in the chambers (table 4). In terms of recovery efficiency, 81.5% of the NH_4-N was recovered during the first week of the experiments, with the remainder being quantitatively recovered by the end of the third week. Interestingly, we found that the NH_3 volatilized from the litter can move down and below the litter layer and be effectively recovered, as shown in the "under" treatment in figure 7a. This finding provides flexibility in future membrane treatment system design. For example, membrane manifolds may be placed below the bedding, or under caged production, thus minimizing exposure of birds to NH_3. Our results also show that aboveground placement of membrane manifolds is equally effective at recovering NH_3 from the litter, and these manifolds could be placed in grids near the

Table 3. Physical properties, mass balance, and NH_3 capture rates of the three ePTFE tubular membranes after 21 days.

Type	Surface Area (cm^2)	Membrane surface to volume ratio (cm^2 cm^{-3})	Total NH_4-N Captured[a] (mg)	Total NH_4-N Lost[b] (mg)	NH_4-N Recovery (%)
A	83.2	10.0	240.2 (3.9)	267.2 (4.0)	89.9
B	108.9	7.6	293.9 (5.2)	287.8 (3.7)	102.1
C	181.5	4.6	266.8 (5.4)	280.1 (6.4)	95.3
Control	n/a	n/a	0.0	102.1 (1.4)	0.0
$LSD_{0.05}$			54.02	69.33	

[a] Total NH_4-N measured in the acid trap after 21 days of incubation. Values are means (standard error of mean shown in parentheses) for duplicate samples (n = 2).

[b] Total NH_4-N in the litter at the end of experiment calculated by subtracting NH_4-N content on day 21 from initial NH_4-N content on day 0. Values are means (standard error of mean shown in parentheses) for duplicate samples (n = 2).

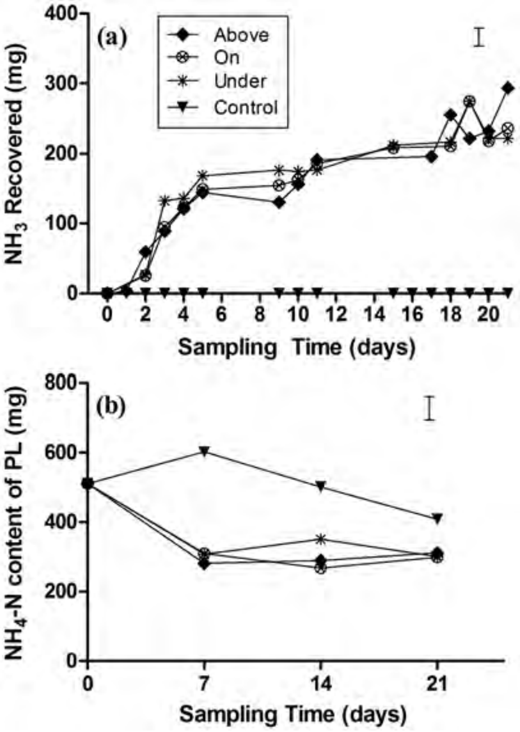

Figure 7. Mass of (a) NH_3 recovered in the acidic solution and (b) NH_4-N remaining in the poultry litter (PL) from chambers comparing the effect of membrane height from litter surface. The controls were run for both the acidic solution and the poultry litter, as described in figure 6. All points are means of duplicate chambers. The bar in the upper right corner of each graph represents the $LSD_{0.05}$ value for the NH_3 recovered in the acidic solution (27.992) and NH_4-N remaining in the litter (63.657).

surface, along waterer/feeder lines, or even on the building walls.

Current NH_3 abatement technologies used in livestock houses rely on the ventilation systems and N treatment of the exhaust air from the house (Melse and Ogink, 2005; Ndegwa et al., 2008), but recent research has shown that NH_3 concentrations close to the litter surface (<20 cm), where the birds are exposed, can be up to one order of magnitude higher than in the bulk house air (Lahav et al., 2008). A significant departure is the concept of Lahav et al. (2008) of removing NH_3 using manifolds that extract only the air close to the litter independent of the house ventilation system. Our approach using a membrane system follows the same concept, in that the NH_3 can be recovered near the litter with potential benefits to bird health and improved productivity, with the additional advantage that NH_3 is passively removed.

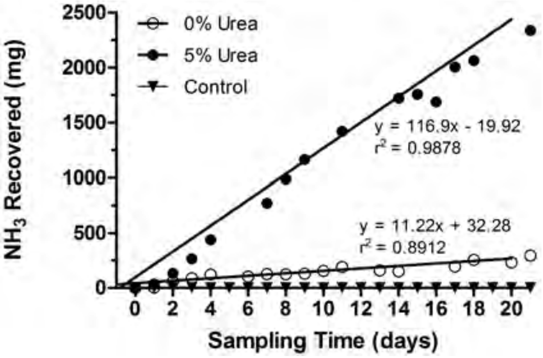

Figure 8. Mass of NH_3 in the acidic solution from chambers amended with (5% w/w) or without urea as a nitrogen source to simulate the nitrogen input to the litter in a poultry house. A control was run for the acidic solution (without poultry litter). All points are means of duplicate chambers.

EXPERIMENT 3: REMOVAL CAPACITY UNDER ENHANCED AMMONIA VOLATILIZATION CONDITIONS

Excess urea (5% total mass) was added to the litter to determine how increased N input affected the NH_4-N mass potentially recovered by the ePTFE membrane system. The amount of urea added was equal to approximately twice the N input of an average broiler over a typical grow-out period (42 to 56 d), assuming 930 cm^2 (1 ft^2) of litter surface area is occupied per broiler. The above calculations assume that, on a dry weight basis, an average broiler produces 37.5 g of manure daily, of which 0.75 g (2% of total mass) is in a nitrogenous form (Naber and Bermudez, 1990). Initially, the total N content of the litter in the 5% urea treatment chamber was 16.39 ±0.86 g, with the urea accounting for 42.8% (7.02 g) of the total N. For comparison, the litter from the non-amended (0%) treatment litter contained 7.33 ±0.31g of total N.

The addition of urea to the litter increased the recovery of NH_3 (2287.4 ±9.2 mg) as compared to the non-amended litter (293.9 ±26.6 mg). The corresponding rate of daily NH_3 capture per unit ePTFE surface area was 10.5 g m^{-2} d^{-1} for the enhanced urea treatment and 1.3 g m^{-2} d^{-1} for the non-amended litter (fig. 8). The rate of NH_3 recovery in the 5% urea treatment (116.9 mg d^{-1}) was significantly ($p < 0.0001$) higher than in the 0% treatments (11.2 mg d^{-1}). These results indicate that the ePTFE system had higher capacity to recover NH_3 than in previous experiments (figs. 6 and 7; tables 3 and 4) and that the limitation in those experiments was the amount of available NH_3. The concentration of NH_4-N in the acidic solution after 21 days was 7859 ±96 mg L^{-1}, or 0.79%.

Table 4. Weekly mass balance and percent recovery of NH_3 from pooled poultry litter samples from the three chambers with ePTFE tubular membranes at varying heights with respect to litter surface.

Sampling Time (days)	NH_4-N Content of Litter[a] (mg kg^{-1})	NH_4-N Mass Loss from Litter[a],[b] (mg)	NH_4-N Mass Recovered in Acid Trap (mg)	NH_4-N Recovery (%)
0	1369.2 (9.2)	0	0	0
7	758.3 (8.2)	211.4 (4.1)	172.3 (3.3)	81.5
14	766.7 (9.9)	208.4 (6.1)	199.7 (3.7)	95.8
21	791.7 (7.2)	207.3 (4.0)	230.0 (3.6)	110.9

[a] Values are means (standard error of the mean in parentheses) of duplicate 2 M KCl extractions of litter from the three treatments (*n* = 3).
[b] Calculated by subtracting mass of NH_4-N at that sampling time from initial mass of NH_4-N in the litter.

In addition to NH_4-N reduction in the litter, the membrane treatment also reduced NH_3 concentrations in the air. Measurements of NH_3 concentrations in the headspace air of the laboratory chamber after seven days showed 1.2 ±0.1 mg L^{-1} NH_3 in the membrane system and 17.5 ±0.2 mg L^{-1} NH_3 in the control chamber without membrane. This represents a 93% reduction in the headspace NH_3 concentrations in the membrane system.

The pH of the acidic solution in the 0% urea treatment was unchanged at day 21 compared to the beginning of the experiment, while the pH of the acidic solution from the 5% urea treatment increased by about 2 pH units (from 0 to 2). This increase in pH indicates a 99% reduction in the available protons (Lahav et al., 2008) in the 5% urea treatment after 21 days as compared to the initial acidic solution and that the acidic solution would have needed to be recharged to recover additional NH_3. Therefore, it is important to keep up with the continuous supply of protons in this type of system so that the acidity is not limiting effective NH_3 recovery. Fortunately, we can use the pH of the acidic solution as an indication of acid recharge needs.

EXPERIMENT 4: ACCELERATED RECOVERY OF AMMONIA WITH MEMBRANE TECHNOLOGY

Hydrated lime [$Ca(OH)_2$] was applied to the litter at three rates (0.4%, 2%, and 4% w/v) to increase the pH of the litter to rapidly transform NH_4-N into NH_3 gas and evaluate treatment time reduction compared to a control treatment (0% $Ca(OH)_2$ addition) (fig. 9, table 5). The addition of 0.4%, 2%, and 4 % (w/v) $Ca(OH)_2$ instantaneously increased the pH of the litter (10.23 ±0.10, 12.69 ±0.01, and 12.81 ±0.10, respectively) as compared to the litter without $Ca(OH)_2$ addition (8.96 ±0.02). As a consequence, the increased NH_3 volatilization due to chemical addition significantly increased NH_3 recovery by the membrane system (fig. 9a). Treatment time was reduced from about 21 days to less than seven days. Ammonia was actively captured until days 7, 3, and 2 for the 0.4%, 2%, and 4% (w/v) treatments, respectively, at which point the recovered NH_3 reached a maximum and no significant additional NH_3 was captured in the acidic solution (fig. 9a). In contrast, the treatment without hydrated lime addition slowly accumulated NH_3 in the acidic solution throughout the entire 21-day experiment. In terms of surface area of the membrane, the rates of NH_3 recovery were 1.29, 4.94, 9.67, and 16.52 g m^{-2} d^{-1} for the 0%, 0.4%, 2%, and 4 % (w/v) $Ca(OH)_2$ additions, respectively. Therefore, the speed of NH_3 recovery by the membranes can be enhanced by increasing the pH of the litter, and commercially available hydrated lime is an effective chemical for this purpose.

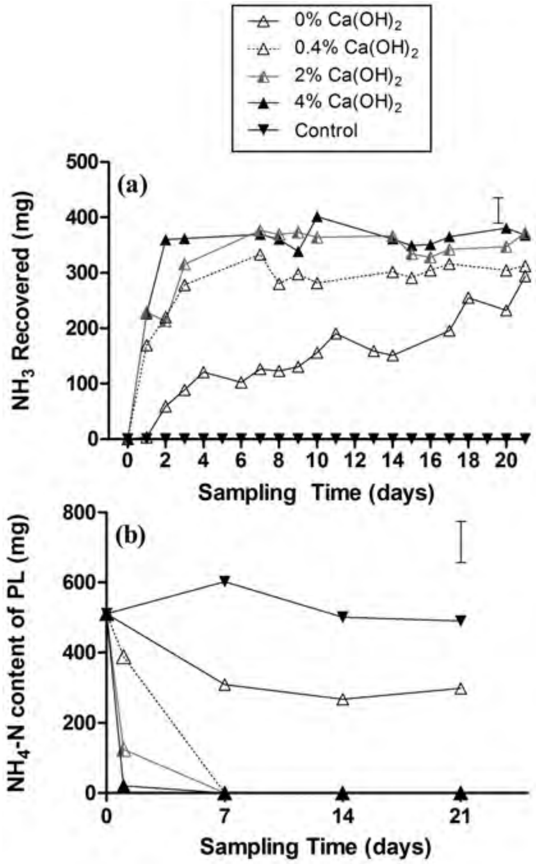

Figure 9. Mass of (a) NH_3 recovered in the acidic solution and (b) NH_4-N remaining in the poultry litter (PL) from chambers amended with hydrated lime ($Ca(OH)_2$). Day 1 litter values in (b) represent initial samples that remained on the bench-top for one day prior to analysis to determine the rapid release of NH_3 from the litter. The controls were run for both the acidic solution and the poultry litter, as described in figure 6. All points are means of duplicate chambers, and the error bar in the upper right corner of each graph represents the $LSD_{0.05}$ value for the NH_3 recovered in the acidic solution (50.711) and NH_4-N remaining in the litter (123.19).

The NH_4-N content of the litter decreased quickly within one day of chemical addition, from 511.0 ±4.7 mg to 388.9 ±5.3, 124.4 ±5.9, and 21.3 ±3.5 mg in the 0.4%, 2%, and 4% (w/v) $Ca(OH)_2$ treatments, respectively (fig. 9b). Corresponding NH_4-N remaining in the litter after one day was 76.1%, 24.3%, and 4.2%. After seven days, the NH_4-N content in the litter of all three chemically amended treatments was zero, indicating complete volatilization. In

Table 5. Mass balance, percent NH_3 recovery, and headspace NH_3 concentrations from poultry litter seven days after addition of three different hydrated lime rates.

Percent Hydrated Lime (w/v)[a]	NH_4-N Mass Loss from Litter (mg)[b],[c]	NH_3 Mass Recovered in Acid Trap (mg)[c]	NH_3 Recovery (%)	NH_3 Headspace Concentration (mg L^{-1}) Without ePTFE[c]	NH_3 Headspace Concentration (mg L^{-1}) With ePTFE[c]
0	202.0 (1.0)	146.3 (2.2)	72.4	8.8 (0.1)	0.2 (0.08)
0.4	511.0 (4.7)	333.0 (5.5)	67.7	34.0 (1.4)	0.0 (0.0)
2	511.0 (4.7)	376.3 (4.9)	73.6	17.8 (1.4)	0.0 (0.0)
4	511.0 (4.7)	389.4 (2.1)	76.2	14.6 (1.6)	0.0 (0.0)
$LSD_{0.05}$	14.55	63.93		7.24	0.02

[a] Percent of the total mass of litter at the beginning of the experiment, based on a litter bulk density of 0.3864 g mL^{-1}.
[b] Calculated by subtracting mass of NH_4-N at day 7 from initial mass of NH_4-N in the litter.
[c] Values are means (standard error of the mean shown in parentheses) of duplicate 2 M KCl extractions of litter.

contrast, the NH_4-N contents remaining in the control and 0% treatment were 602.0 ±1.3 and 202.0 ±1.0 mg, respectively (fig. 9b).

The rapid flush of NH_3 by chemical addition exceeded the capacity of the membrane used in the bench-scale chamber, resulting in lower NH_3 recoveries (68% to 76%) after seven days (table 5). For example, the membrane capacity in the 4% (w/v) lime treatments in the first two days was 180 mg d^{-1} (fig. 9a), which is lower than the 490 mg of NH_3 released the first day after chemical addition (fig. 9b). Therefore, it is important to consider the NH_3 release dynamics to dimension the size of the membrane system because NH_3 release may be substantially different with natural or chemically enhanced systems.

The use of a membrane system resulted in consistent decreases in headspace NH_3 concentrations for all four treatments as compared to the controls without membranes (table 5, columns 5 and 6). Concentrations of NH_3 in the air were significantly ($p < 0.0001$) reduced from between 8.8 and 34.0 mg L^{-1} to between 0.2 and 0.0 mg L^{-1} (97.7% to 100% reduction).

An additional benefit of the use of hydrated lime is the disinfection of the poultry house. Lime has been shown to effectively destroy or inactivate bacterial and viral pathogens in poultry production facilities, including *Salmonella enteritidis* (Bennett et al., 2003) and H5N1 virus (causative agent of avian influenza; De Benedistis et al., 2007). Therefore, producers choosing to disinfect their houses using lime could benefit from this membrane system by recovering the NH_3 rapidly released from the litter upon lime application.

CONCLUSIONS

The results of this study showed that the concept of using gas-permeable membrane systems to recover NH_3 from poultry litter is technically feasible. On average, these systems recovered 96% of the NH_4-N volatilized from the litter. High NH_3 recoveries were obtained regardless of the positioning of the membrane system above or below the litter surface, providing flexibility in future design and implementation of this system in a poultry house. In addition to efficiently recovering the NH_3 lost from the litter, the membrane system also significantly reduced NH_3 concentrations in the air. We also observed that the speed of NH_3 recovery by the membranes can be enhanced by increasing the pH of the litter and that hydrated lime is an effective chemical for this purpose. Benefits of the technology include cleaner air, reduced NH_3 emissions, and the recovery of NH_3 into a concentrated ammonium salt, allowing the farmer/producer to convert a potential waste (NH_3 gas) into a value-added product (ammonium salt fertilizer).

ACKNOWLEDGEMENTS

The authors would like to thank Aprel Ellison, Jennifer Hemingway, and Kirsten Hiortdahl for their assistance in chamber fabrication, litter sample preparation, and sample analysis. This research was part of USDA-ARS National Program 206: Manure and By-Product Utilization: ARS Project 6657-13630-003-00D "Innovative Animal Manure Treatment Technologies for Enhanced Environmental Quality."

REFERENCES

APHA. 1998. *Standard Methods for the Examination of Water and Wastewater.* 20th ed. Washington, D.C.: American Public Health Association.

Bennett, D. D., S. E. Higgins, R. W. Moore, R. Beltran, D. J. Caldwell, J. A. Byrd II, and B. M. Hargis. 2003. Effect of lime on *Salmonella enteritidis* survival in vitro. *J. Applied Poultry Res.* 12(1): 65-68.

Blet, V., M.-N. Pons, and J. L. Greffe. 1989. Separation of ammonia with a gas-permeable tubular membrane. *Analytica Chimica Acta* 219: 309-311.

Cook, K. L., M. J. Rothrock Jr., J. G. Warren, K. R. Sistani, and P. A. Moore, Jr. 2008. Effect of alum treatment on the concentration of total and ureolytic microorganisms in poultry litter. *J. Environ. Qual.* 37(6): 2360-2367.

Dawkins, M. S., C. A. Donnelly, and T. A. Jones. 2004. Chicken welfare is influenced more by housing conditions than by stocking density. *Nature* 427(6972): 342-344.

De Benedistis, P., M. S. Beato, and I. Capua. 2007. Inactivation of avian influenza viruses by chemical agents and physical conditions: A review. *Zoonoses Public Health* 54(2): 51-68.

Edwards, D. R., and T. C. Daniel. 1992. Environmental impacts of on-farm poultry waste disposal: A review. *Bioresource Tech.* 41(1): 9-33.

Kirychuk, S. P., J. A. Dosman, J. S. Reynolds, P. Willson, A. Senthilselvan, J. J. R. Feddes, H. L. Classen, and W. Guenter. 2006. Total dust and endotoxin in poultry operations: Comparison between cage and floor housing and respiratory effects in workers. *J. Occup. and Environ. Med.* 48(7): 741-748.

Lahav, O., T. Mor, A. J. Heber, S. Molchanov, J. C. Ramirez, C. Li, and D. M. Broday. 2008. A new approach for minimizing ammonia emissions from poultry houses. *Water Air Soil Pollution* 191: 183-197.

Lee, K. C., and B. E. Rittmann. 2000. A novel hollow-fiber membrane biofilm reactor for autohydrogenotrphoic denitrification of drinking water. *Water Sci. Tech.* 41(4-5): 219-226.

Melse, R. W., and N. W. M. Ogink. 2005. Air scrubbing techniques for ammonia and odor reduction at livestock operations: Review of on-farm research in the Netherlands. *Trans. ASABE* 48(6): 2303-2313.

Moore, Jr., P. A., T. C. Daniel, D. R. Edwards, and D. M. Miller. 1995. Effect of chemical amendments on ammonia volatilization from poultry litter. *J. Environ. Qual.* 24(2): 293-300.

Moore, Jr., P. A., T. C. Daniel, and D. R. Edwards. 2000. Reducing phosphorus runoff and inhibiting ammonia loss from poultry manure with aluminum sulfate. *J. Environ. Qual.* 29(1): 37-49.

Naber, E. C., and A. J. Bermudez. 1990. Poultry manure management and utilization problems and opportunities. Bulletin No. 804. Columbus, Ohio: Ohio State University Extension.

Ndegwa, P. M., A. N. Hristov, J. Arogo, and R. E. Sheffield. 2008. A review of ammonia emission mitigation techniques for concentrated animal feeding operations. *Biosystems Eng.* 100(4): 453-469.

Pagans, E., X. Font, and A. Sachez. 2005. Biofiltrations for ammonia removal from composting exhaust gases. *Chem. Eng. J.* 113(2-3): 105-110.

Peters, J., A. Wolf, and N. Wolf. 2003. Ammonium nitrogen. In *Recommended Methods of Manure Analysis*, 25-29. J. Peters, ed. Madison, Wisc.: University of Wisconsin Extension.

Poach, M. E., P. G. Hunt, G. B. Reddy, K. C. Stone, T. A. Matheny, M. H. Johnson, and E. J. Sadler. 2004. Ammonia volatilization from marsh-pond-marsh constructed wetlands treating swine wastewater. *J. Environ. Qual.* 33(3): 884-851.

Pote, D. H., and T. C. Daniel. 2000. Analyzing for total phosphorus and total dissolved phosphorus in water samples. In *Methods of Phosphorus Analysis for Soils, Sediments, Residuals, and Water,* 94-97. G. M. Pierzynski, ed. Southern Cooperative Series Bulletin No. 396. Manhattan, Kans.: Kansas State University.

Ritz, C. W., B. D. Fairchild, and M. P. Lacy. 2004. Implications of ammonia production and emissions from commercial poultry facilities: A review. *J. Applied Poultry Res.* 13(4): 684-692.

Rothrock, M. J., Jr., K. L. Cook, J. G. Warren, and K. Sistani. 2008. The effect of alum addition on poultry litter microbial communities. *Poultry Sci.* 87(8): 1493-1503.

Rylander, R., and M. F. Carvalheiro. 2006. Airways inflammation among workers in poultry houses. *Intl. Archives of Occup. and Environ. Health* 79(6): 487-490.

Shah, S., P. Westerman, and J. Parsons. 2006. *Poultry Litter Amendments.* Raleigh, N.C.: North Carolina State University.

Shindo, M., T. Yamamoto, and K. Kamada. 1981. *Gas Transfer Process with Hollow Fiber Membrane.* Tokyo, Japan: Mitsubishi Rayon, Co., Ltd.

Szögi, A. A., M. B. Vanotti, and M. J. Rothrock Jr. 2010. System and method for reducing gaseous ammonia from animal production and composting systems and for its recovery. U.S. Provisional Patent Application, Washington, D.C. U.S. Patent and Trademark Office SN 61/314,683.

Wheeler, E. F., K. D. Casey, R. S. Gates, H. Xin, J. S. Zajaczkowski, P. A. Topper, Y. Liang, and A. J. Pescatore. 2006. Ammonia emissions from twelve U.S. broiler chicken houses. *Trans. ASABE* 49(5): 1495-1512.

Wing, S., and S. Wolf. 2000. Intensive livestock operations, health, and quality of life among eastern North Carolina residents. *Environ. Health Perspectives* 108(3): 233-238.

Yahav, S. 2004. Ammonia affects performance and thermoregulation of male broiler chickens. *Animal Res.* 53(4): 289-293.

Yushok, W., and F. E. Bear. 1948. Poultry manure: Its preservation, deodorization, and disinfection. Bulletin No. 707. New Brunswick, N.J.: New Jersey Agricultural Experiment Station.