USDA Agricultural Research Service

Ammonia Recovery in Manure Management Systems using Gas-Permeable Membrane Technology

NRCS Webinar, August 25, 2014

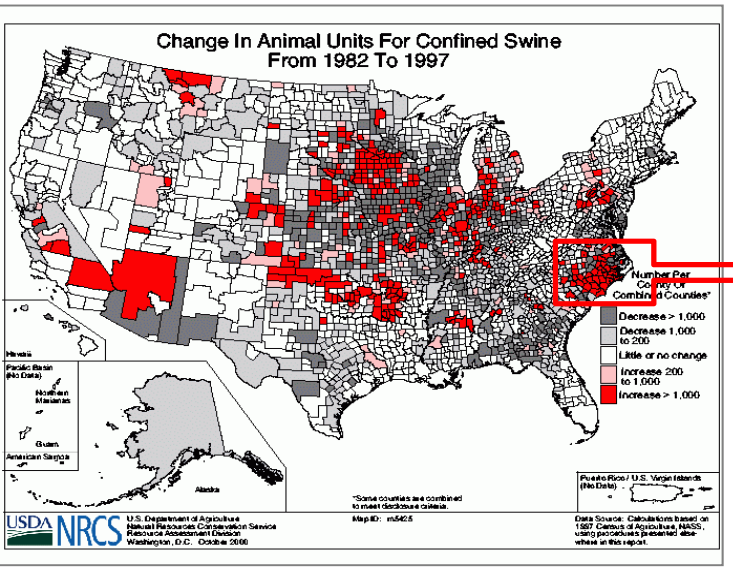
Livestock Gracenet Technology Transfer Series

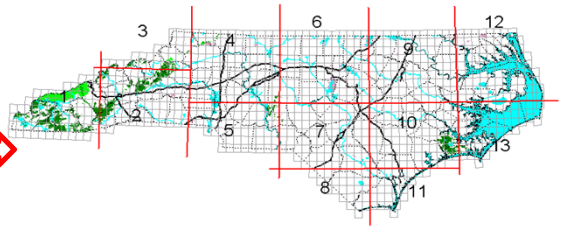
Matias Vanotti and Ariel Szogi

USDA-ARS Coastal Plains Research Center

Florence, South Carolina, USA

Animal Manure – Surplus N and Ammonia Emissions in many regions of USA (and the world)

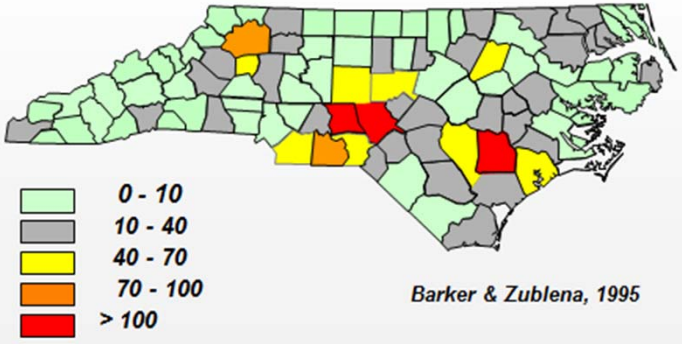




North Carolina produces approximately 750 million chickens, 40 million turkeys, 3.5 billion table eggs, and 19 million hogs per year.

SURPLUS N

Percent of Agronomic Crop and Forage Nitrogen Needs Supplied by Recoverable Plant Available Manure Nitrogen at the County Level in North Carolina



Barker & Zublena, 1995

Ammonia Emissions

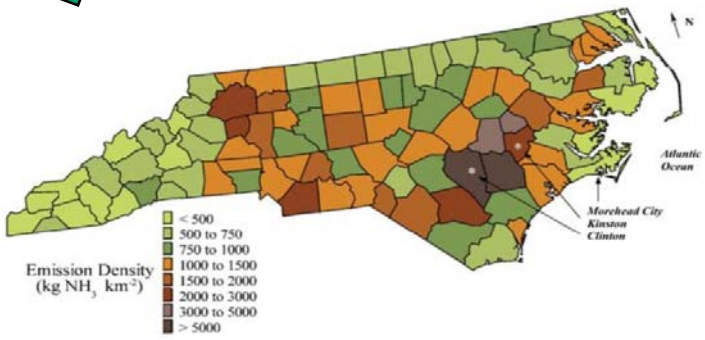


Fig. 1. County scale NH_3 emission density for North Carolina along with measurement sites. Livestock activity data represent 2000 levels. All other activity data represent 1996 levels.

Walker et al., Atmos. Environ. 38:1235-1246

Treatment Technologies for Nitrogen Management in Liquid Manure

1. Biological nitrogen removal
   (conversion of ammonia into N_2)

Nitrification-Denitrification

(Carbon needed)

Anammox deammonification

(Carbon not needed)

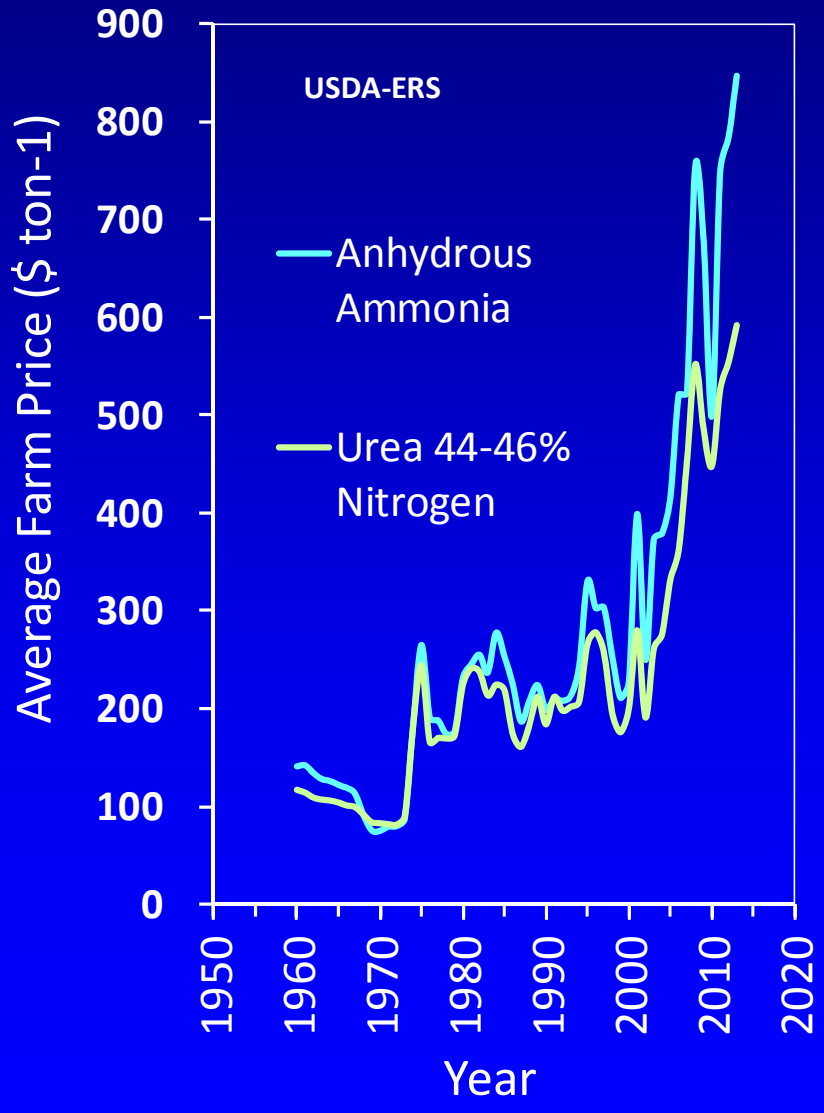
Treatment Technologies for Nitrogen Management in Liquid Manure

1. Biological nitrogen removal
   (conversion of ammonia into N_2)

2. Ammonia removal and recovery

Why recover N?

Escalating U.S. Fertilizer Costs



Why recover N?

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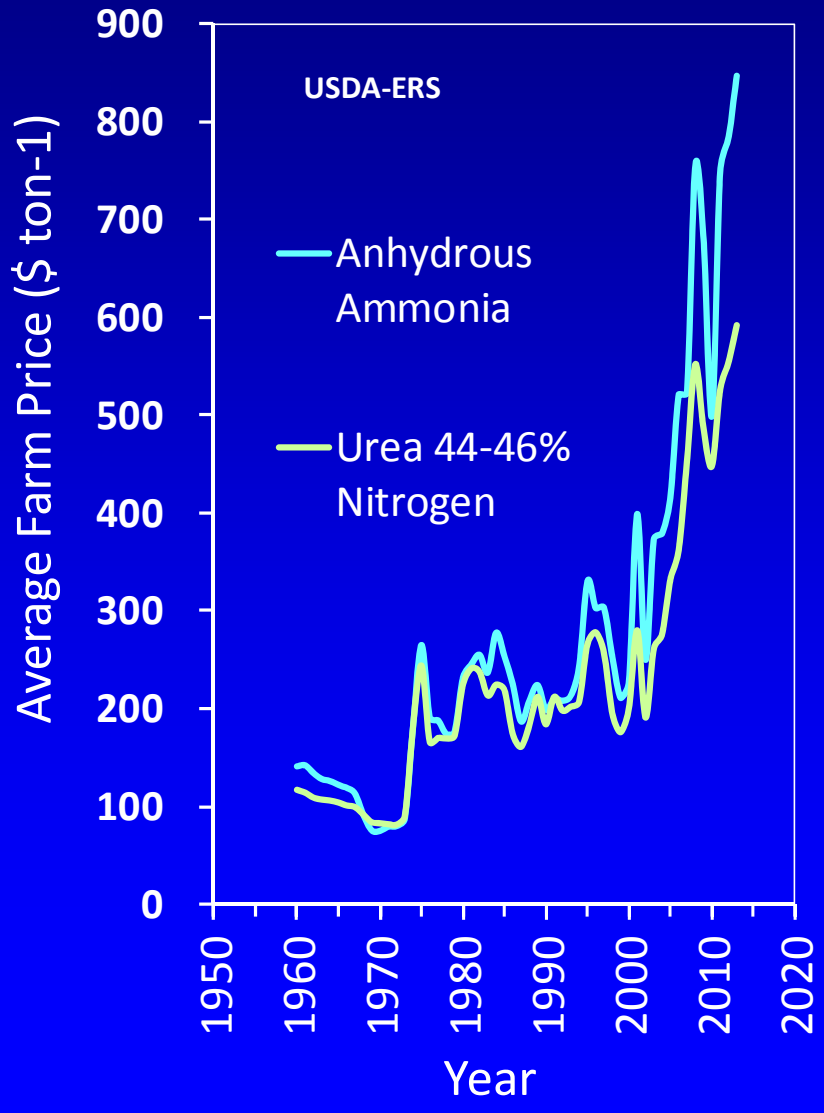
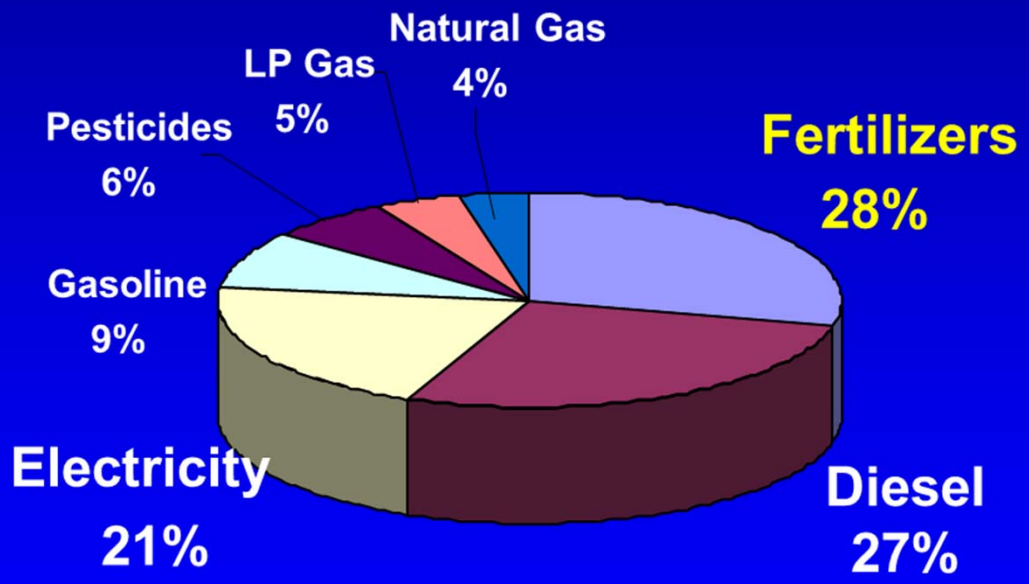
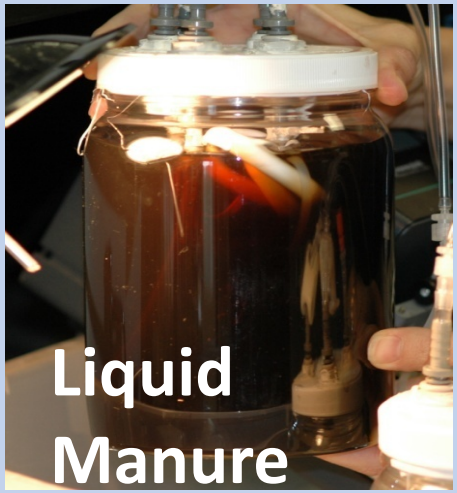


Energy and Agriculture



New: Recovery of Ammonia from Manure



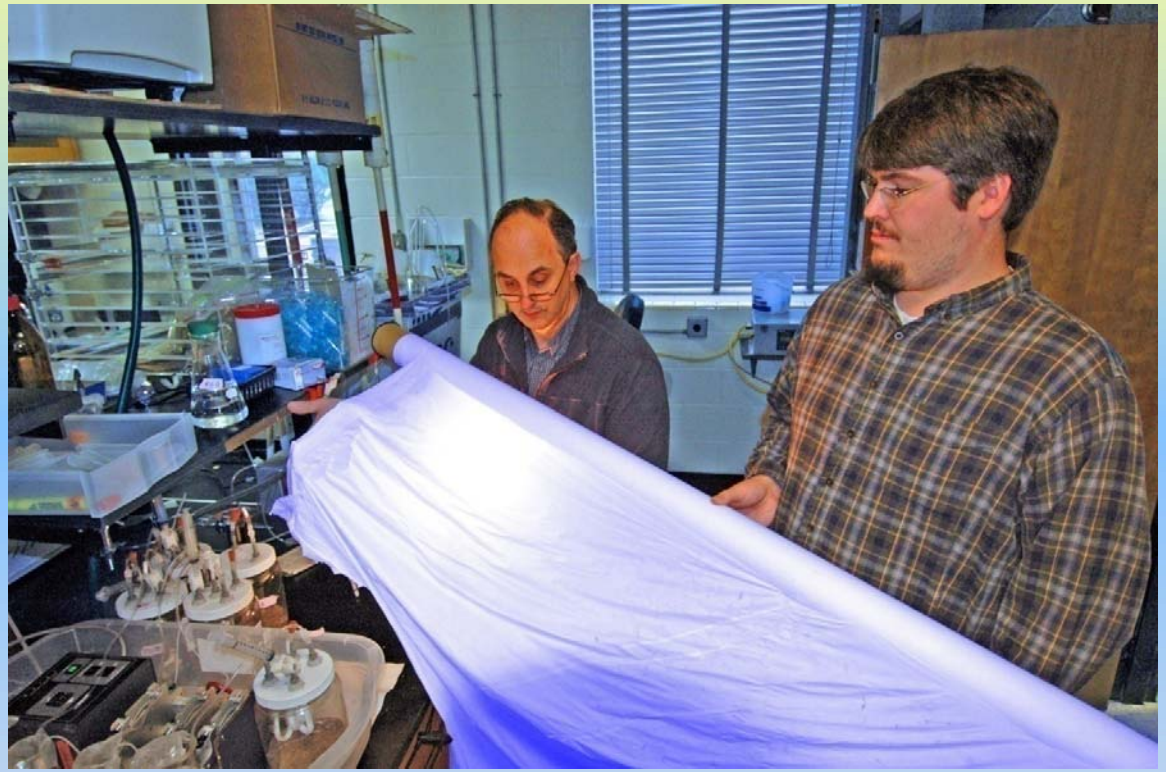
- ❑ Ammonia is separated using gas-permeable membranes
- ❑ Applications include liquid manures and air in livestock houses
- ❑ Product is liquid fertilizer with 50,000 to 100,000 ppm N

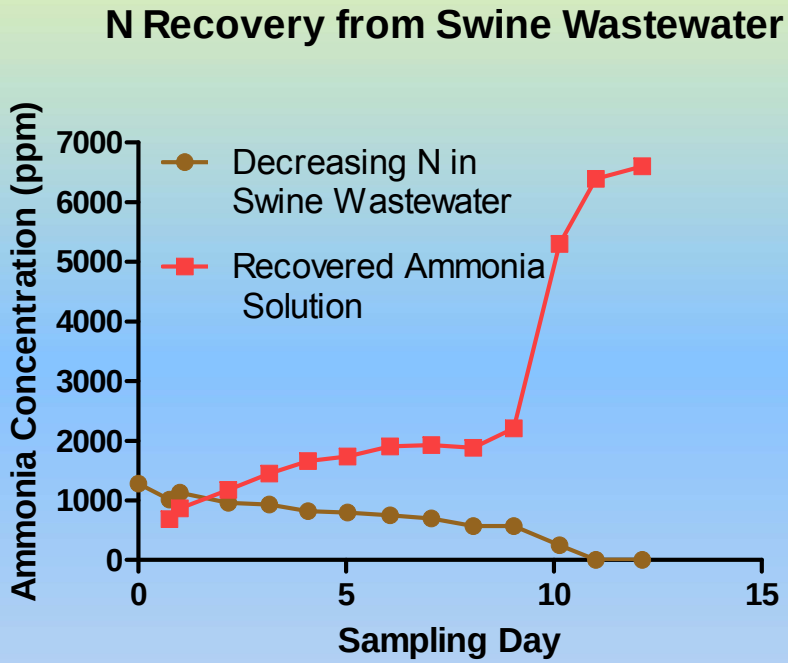
USDA filed two US patents for recovery of ammonia from manure using gas-permeable membranes

- Liquid manure: "Systems and Methods for Reducing Ammonia Emissions form Liquid Effluents and for Recovering Ammonia. US Patent Application SN 13/164,363, filed June 20, 2011 (Vanotti,M.B., and Szogi,A.A.)"

- Air in barns : "Gaseous ammonia removal system. US Patent Application SN 13/048,375, filed March 3, 2011. (Szogi,A.A., Vanotti,M.B., and Rothrock,M.J. Jr.)". (USPTO #20110229403**)**.

Recovery and Concentration of Ammonia





- **Ammonia permeation through microporous, hydrophobic membranes**
- **Reduced ammonia emissions from livestock operations**
- **Product is ammonia solution with > 50,000 ppm N**

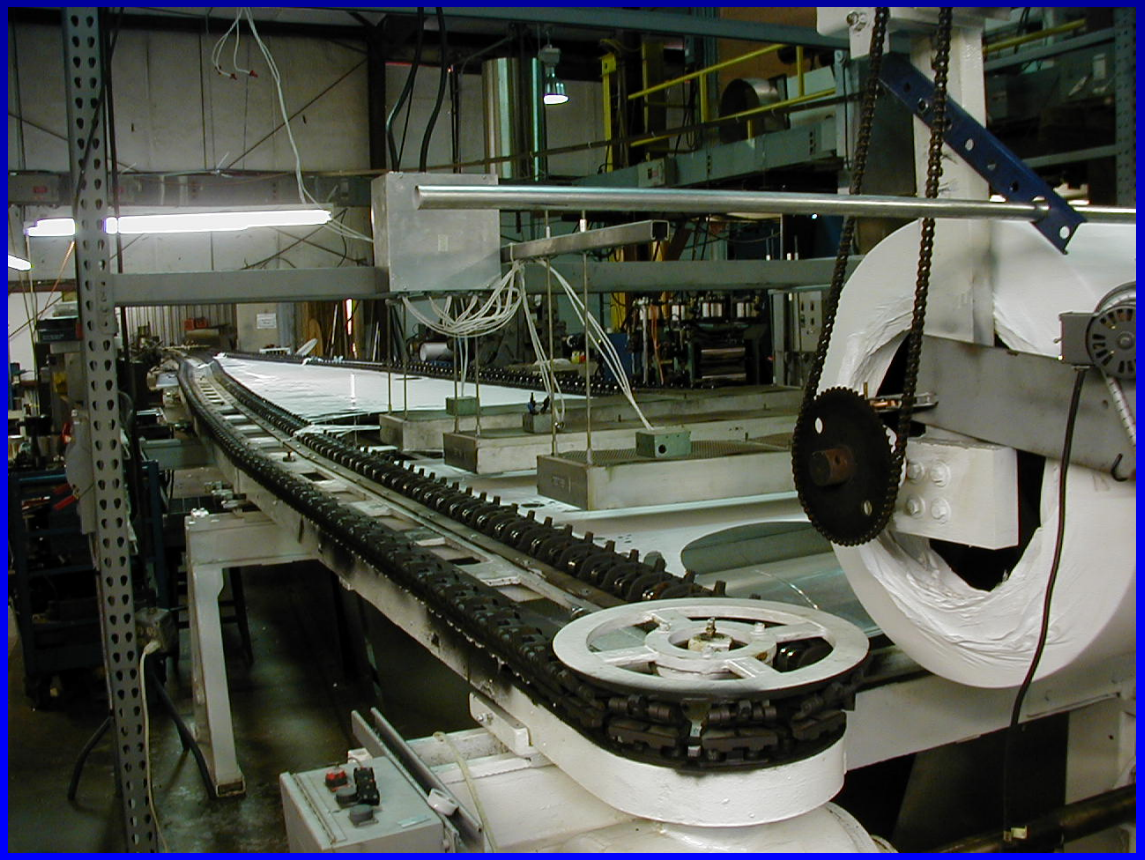
Earlier uses of Gas-permeable membranes

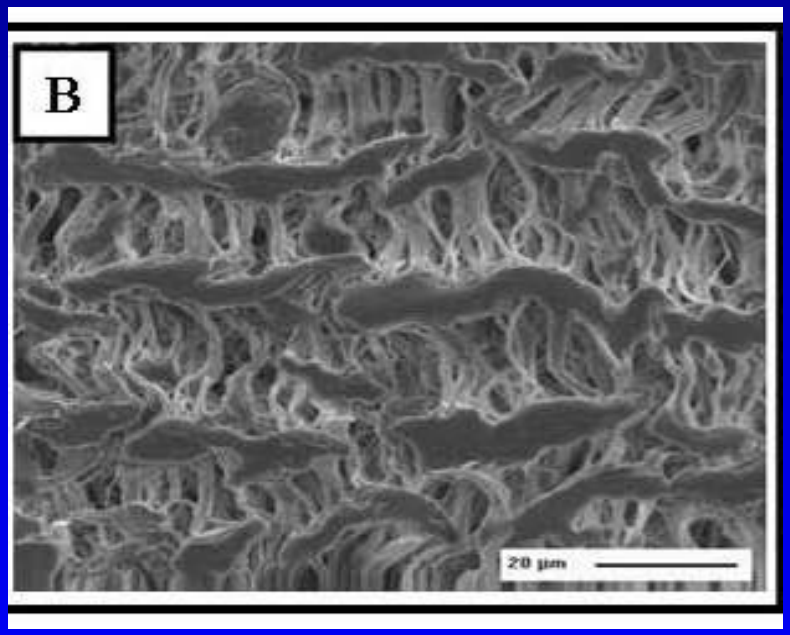
- **Medical uses:** Used in cardiopulmonary bypass, to add oxygen to, and to remove carbon dioxide from the blood (Gaylor, 1988).

- **Clothing & shoe industries:** Used to provide breathable fabrics in sportswear and footware (i.e. *GORE-TEX® Products, 1968)*
- **Desalination of water**: Used in membrane distillation (MD) reactors to purify water.

For this research we used gas-permeable membranes made of <u>expanded</u> polytetrafluoroethylene (ePTFE)

PTFE is stretched to form a strong, porous material





Gas Permeable Membrane
Microscopic structure (SEM)

Manufacture of Gas Permeable Membrane in South Carolina

Presentation Outline

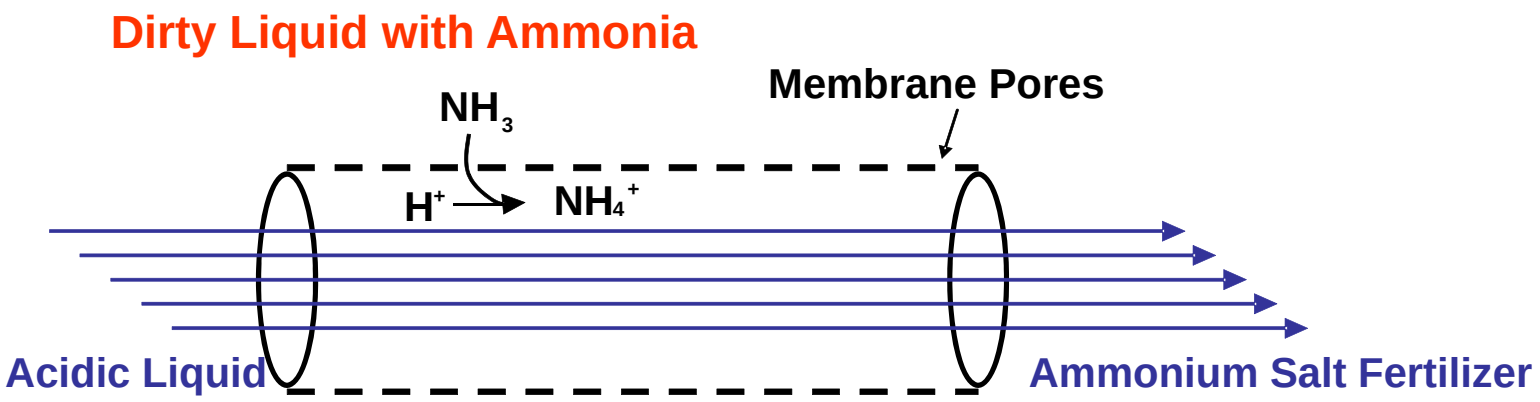
1) Ammonia Recovery from Liquid Manure
2) Ammonia Recovery from Air in Barns

WHAT IS INTENDED TO DO?

- Removal of ammonia gas from the liquid manures before it escapes into the air.
- Nitrogen is recovered from liquid manures in a concentrated, purified form

How does it work?

Concept of Ammonia Capture from Wastewater using Gas Permeable Membrane



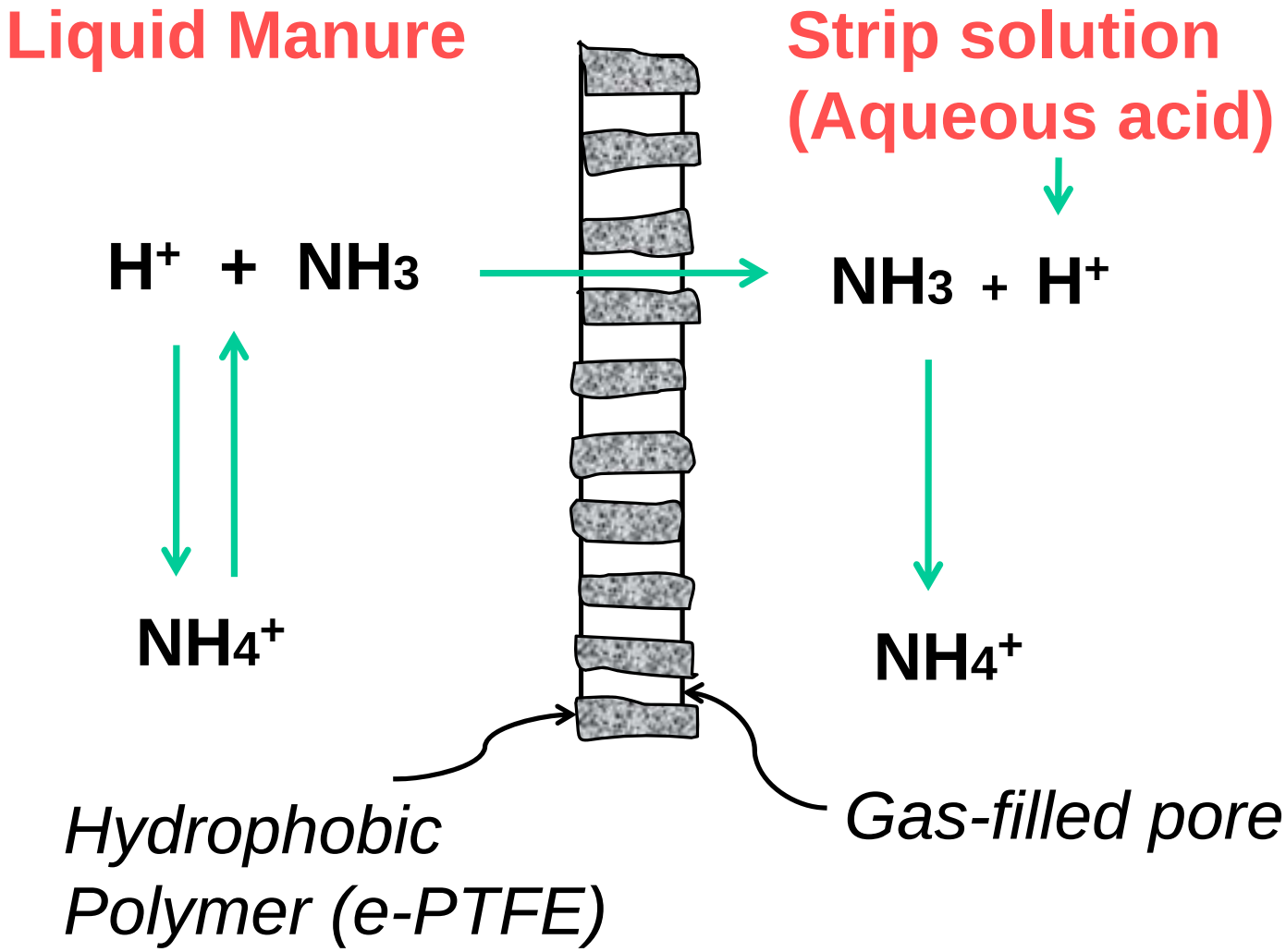
Tubular or Flat Membrane Manifold Submerged in the Wastewater

TUBULAR MEMBRANES

Removal of NH_3 from Liquid Manure Using Gas-Permeable Membranes

Gas-permeable membrane system:

The ammonia gas (NH3) passes through

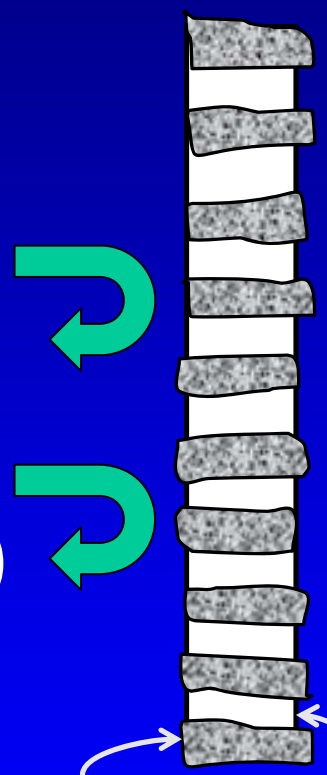


Microporous gas-permeable membrane :
In tests, the soluble carbon did not pass through

Synthetic Wastewater

Glucose (500 ppm COD)

KHP (1000 ppm COD)



Strip solution (water)

H_2O

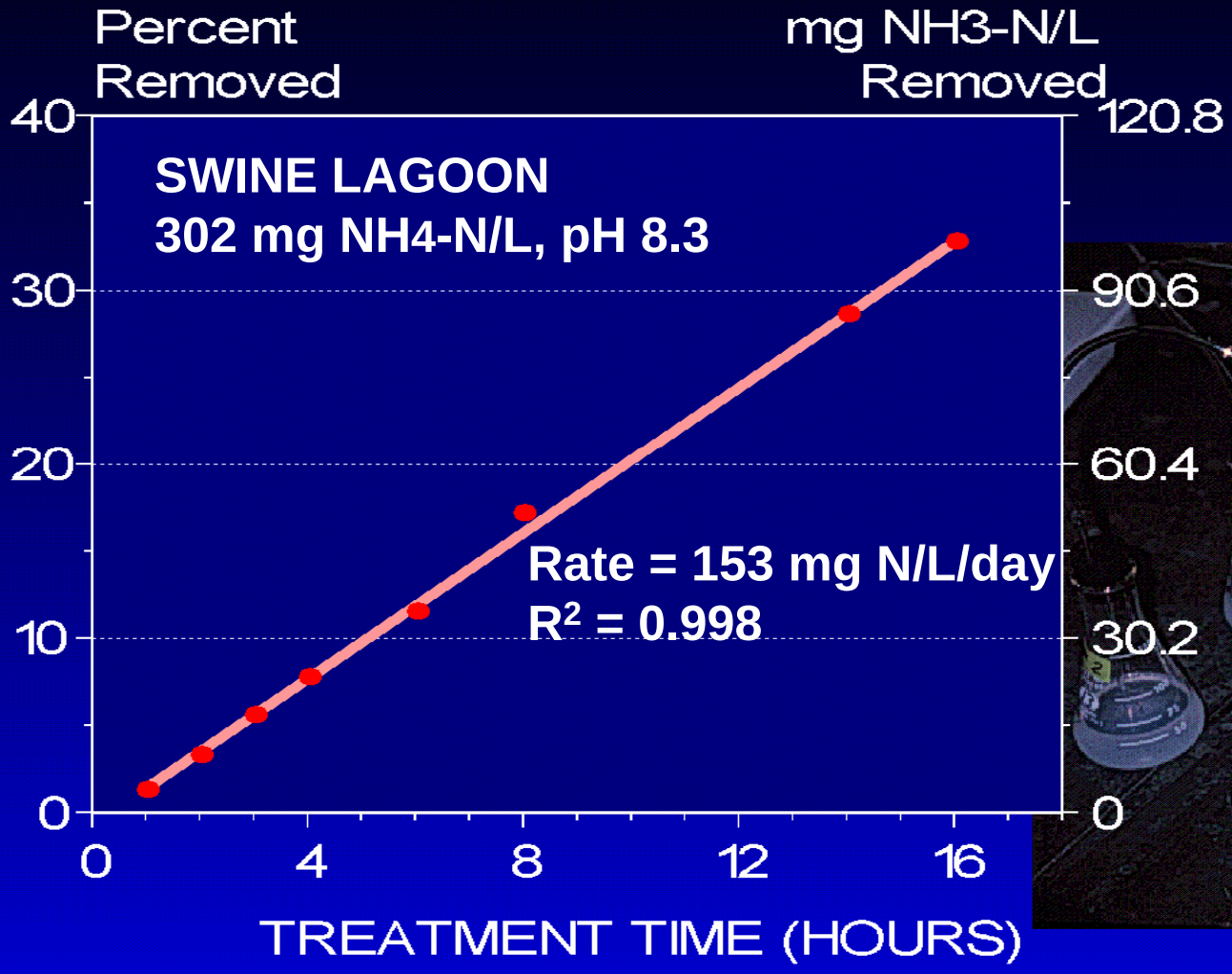
0 ppm COD

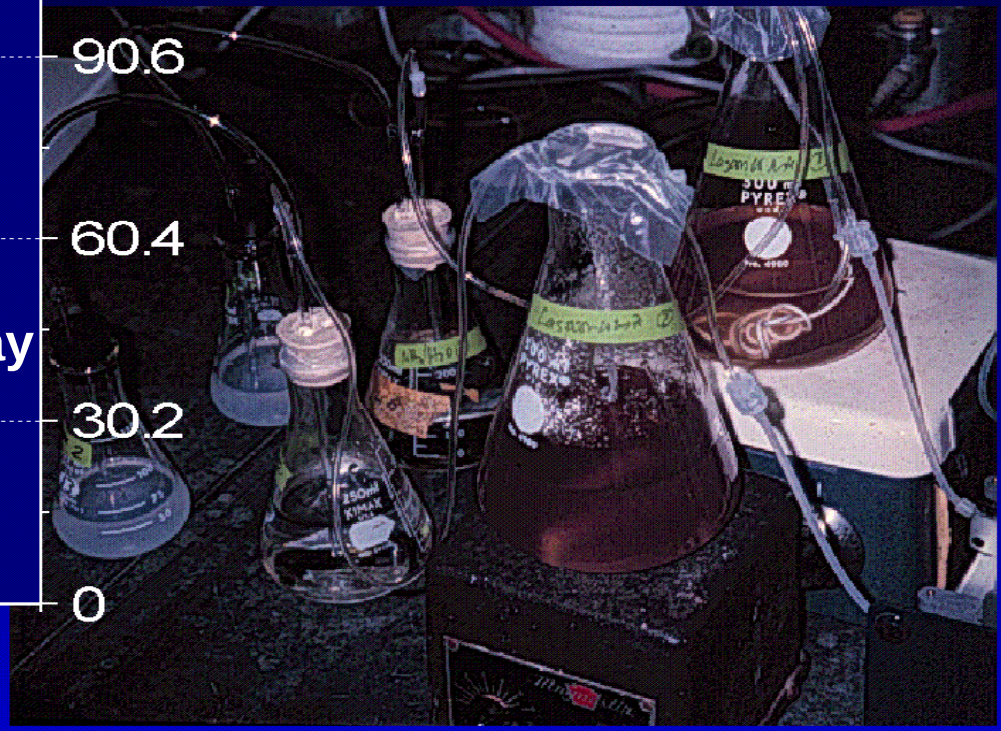
Hydrophobic Polymer (e-PTFE)

Gas-filled pore

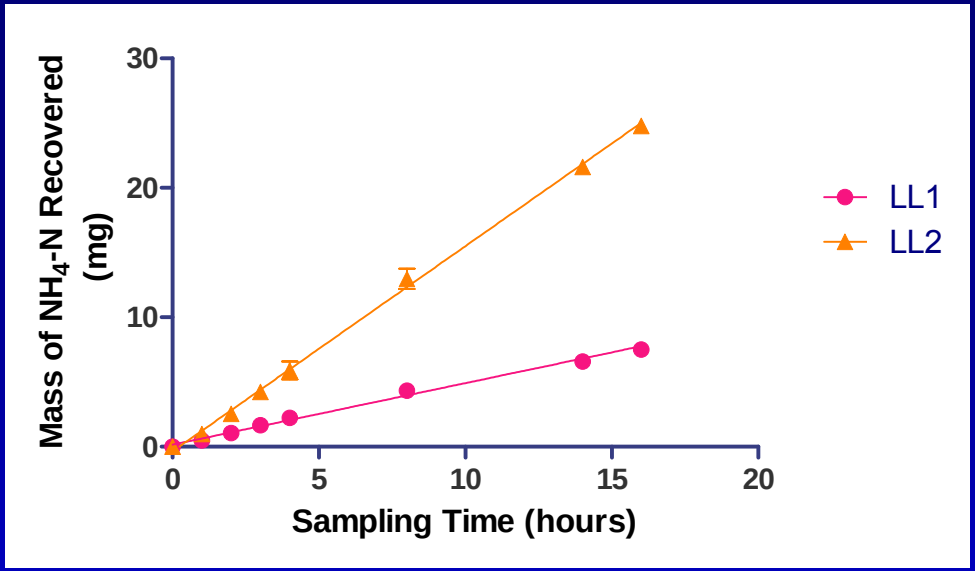
Does it work?

Ammonia removal from animal waste using gas permeable membranes



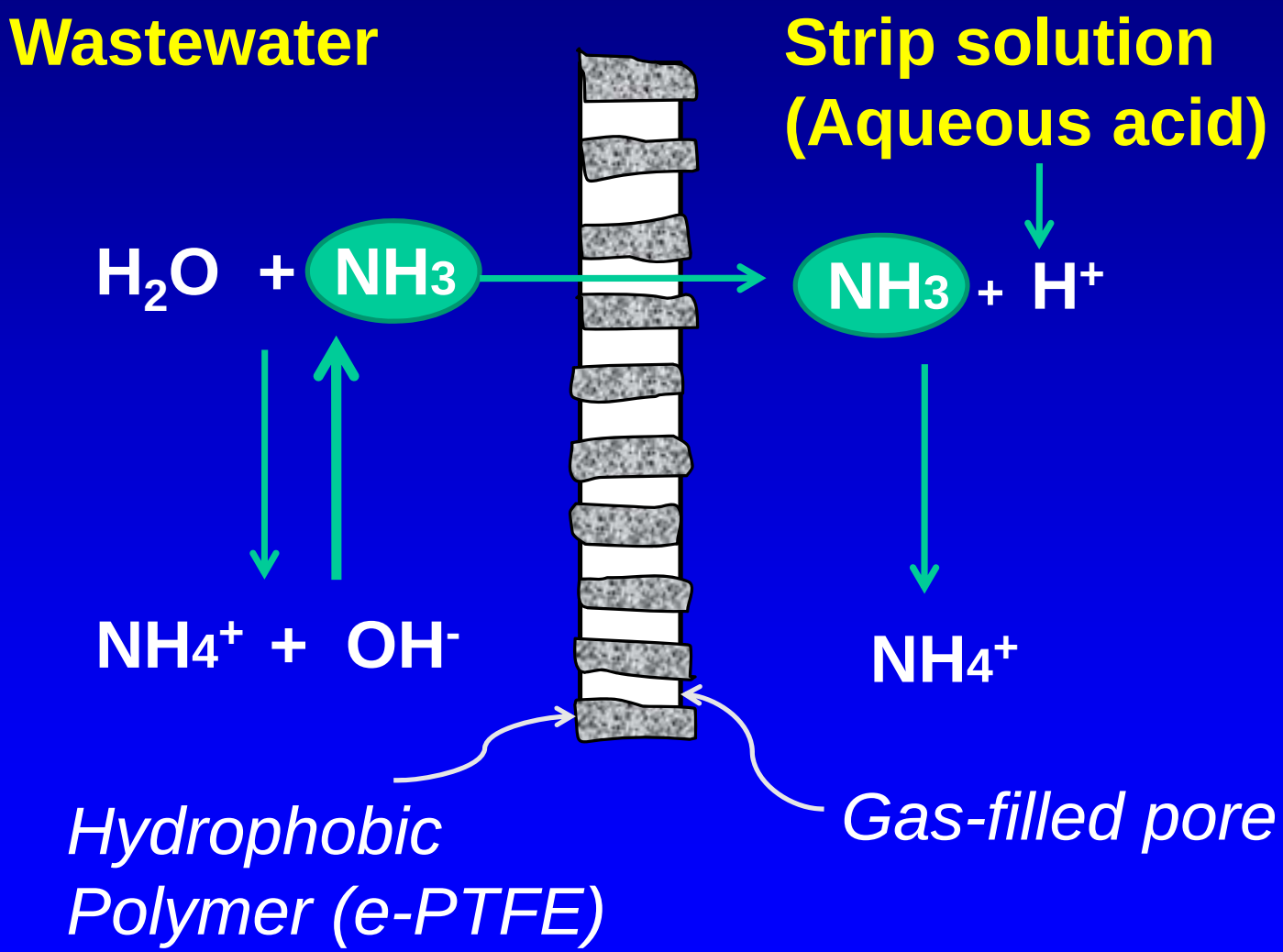


With increased NH_4^+ concentration, the removal rate was higher



	Lagoon liquid 1	Lagoon liquid 2
Liquid pH	8.4	8.3
NH_4-N concentration	138 mg N /L	302 mg N/ L
Mass N in reactor	34.5 mg N	75.5 mg N
Mass N recovered (16 hours)	7.4 mg N	25 mg N
Removal rate	45 mg N / L / day	153 mg N / L / day

Gas-permeable membrane used for separation of free ammonia (NH_3)



Design Parameter: Effect of wastewater pH:

Time (hours)	Initial Source pH = 8.3			Initial Source pH = 10.0		
	Mass NH_4-N in Trap (mg)	NH_4-N Recovery from Source (%)	pH of Trap	Mass NH_4-N in Trap (mg)	NH_4-N Recovery from Source (%)	pH of Trap
0	0	**0**	1.08	0	**0**	1.08
1	0.86	**1.0**	1.11	7.82	**8.7**	0.99
2	2.44	**2.7**	0.98	26.51	**29.4**	1.16
3	3.72	**4.1**	0.99	38.60	**42.9**	1.28
4	4.77	**5.3**	1.1	48.86	**54.3**	1.6
5	5.39	**6.0**	1.0	56.40	**62.7**	1.8

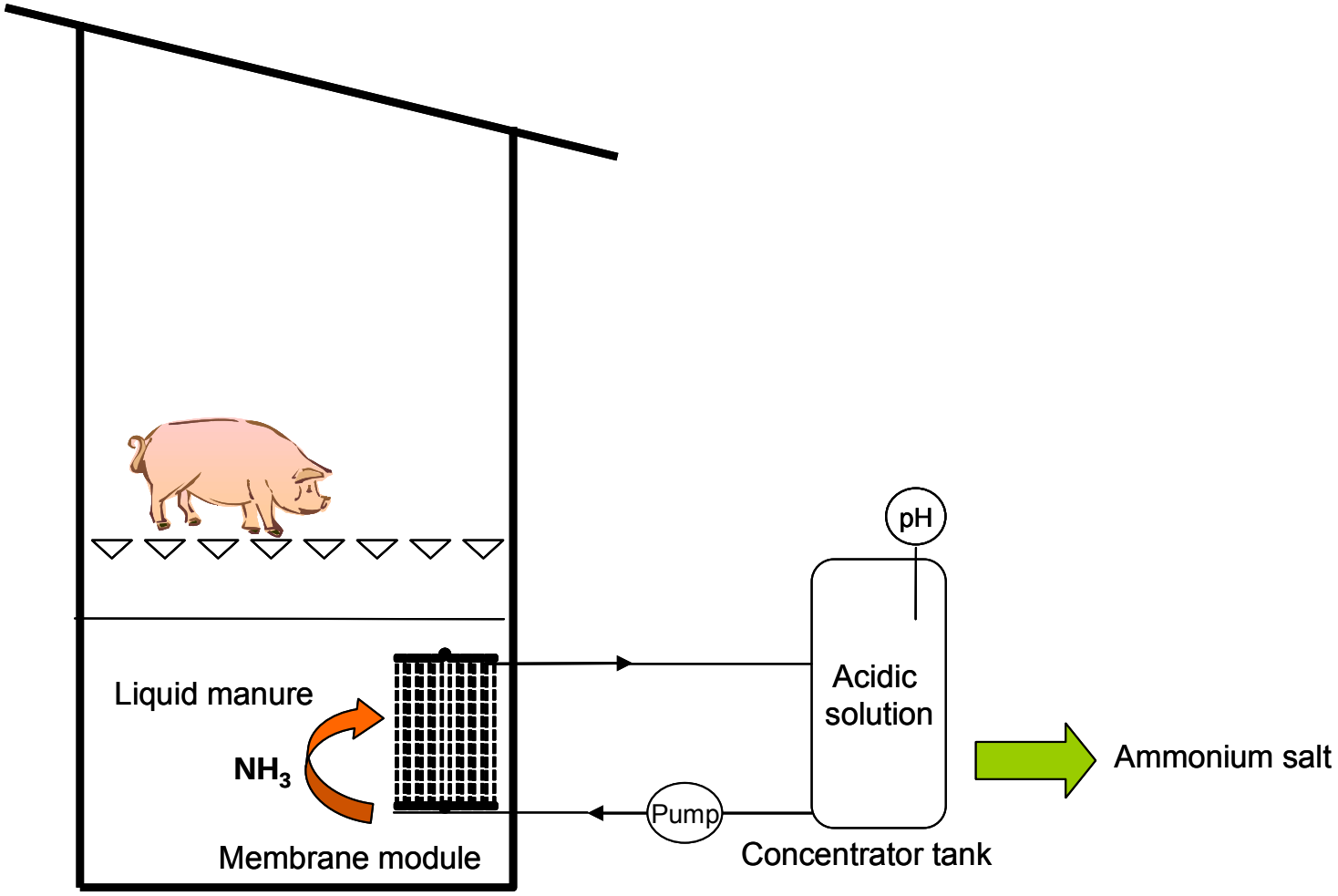
N Recovery was ~ 1.2 % per hour at pH 8.3 and 13% per hour at pH 10 (increased 10 times)

Design Parameter: Effect of waste strength

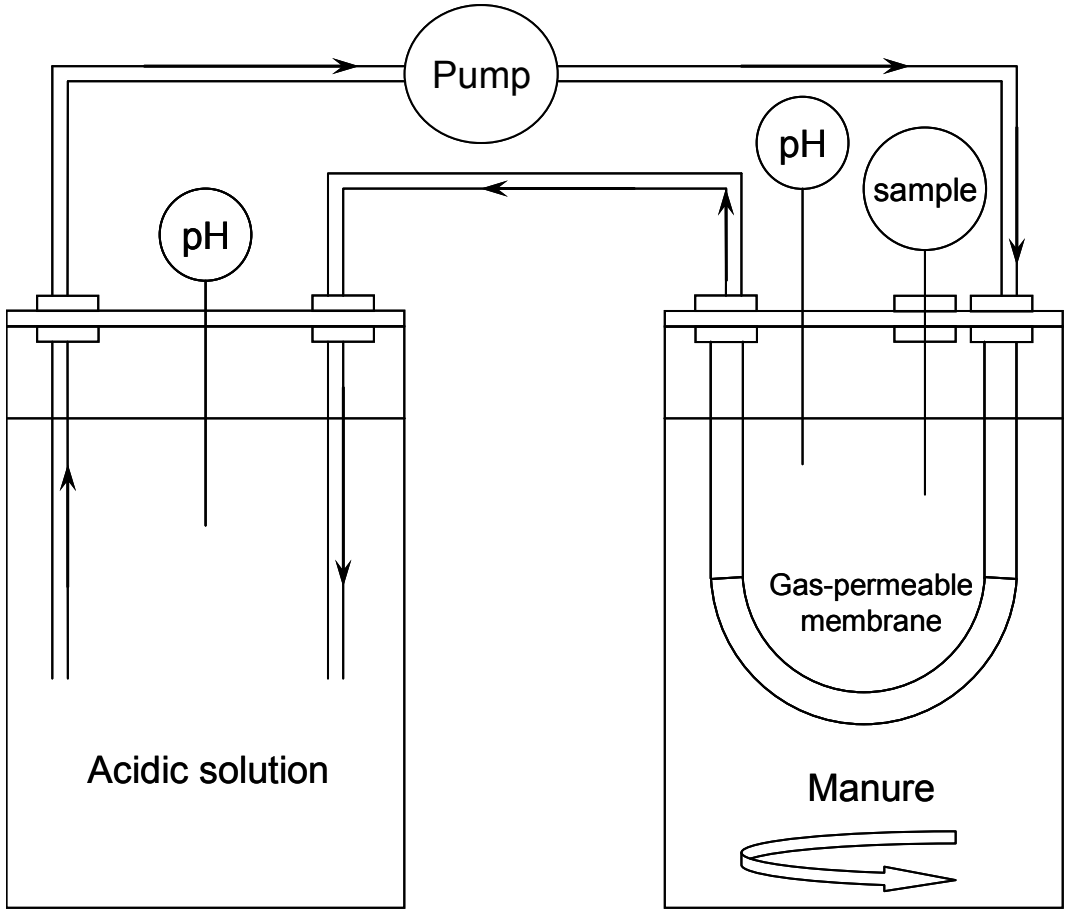
Swine manure characteristics

Manure strength	Swine Farm Type	pH	NH_4-N mg/l	TKN mg/L	EC (mS)	COD mg/L	TS g/L	VS g/L
Low	Piglet	8.64	1065	1345	8.470	4519	4.89	2.58
Medium	Farrow-finish w/ separation	7.57	1680	2743	14.080	24405	17.41	10.33
High	Finishing	7.52	2285	3699	16.980	34081	29.87	20.13

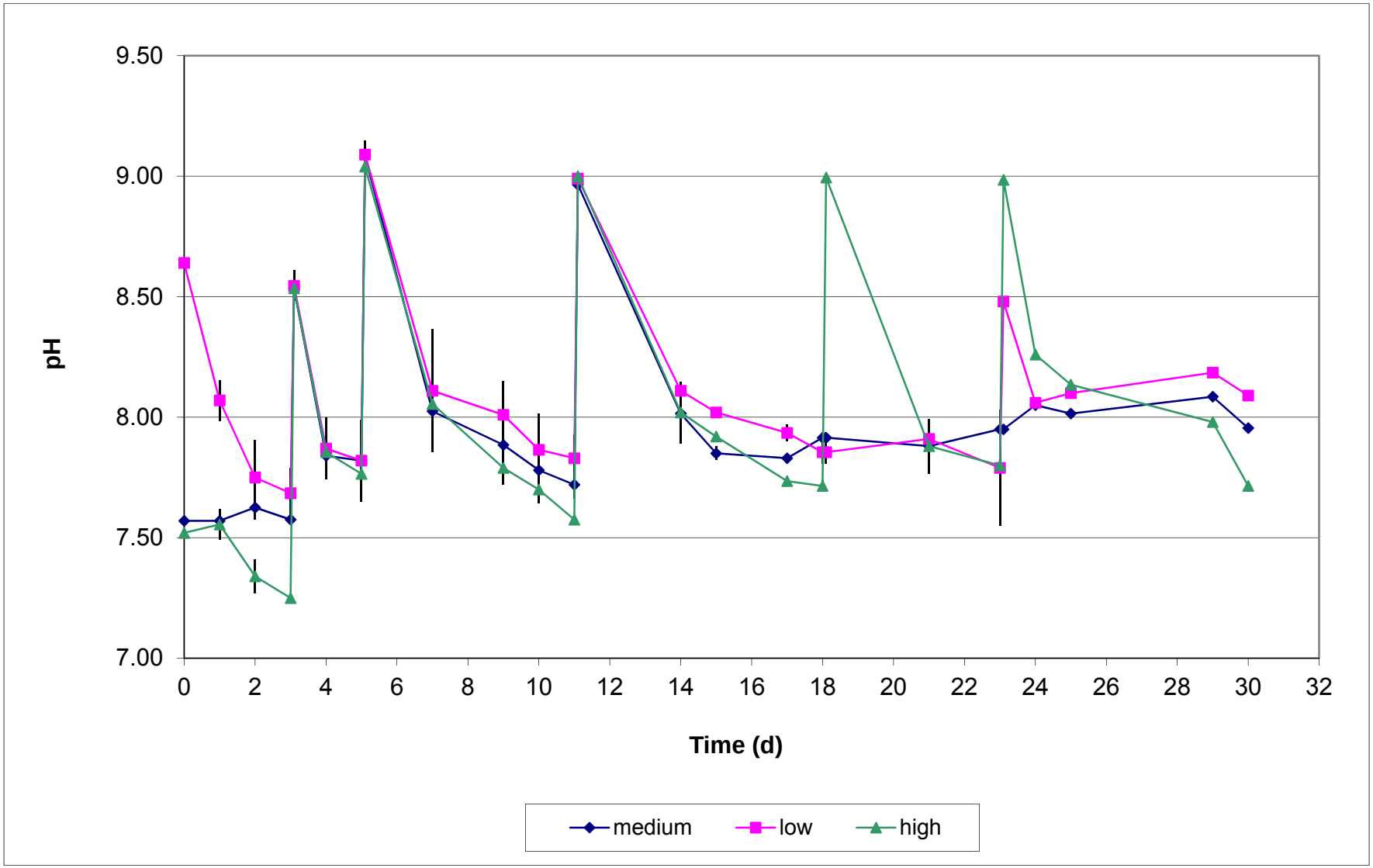
Ammonia recovery from livestock manure using gas-permeable membrane module and concentrator tank (Closed loop system).



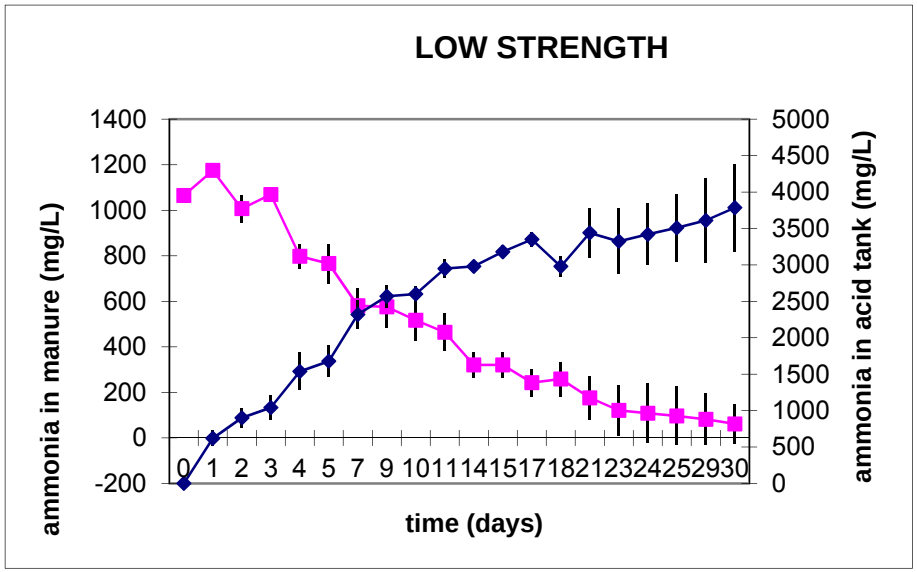
Experimental device for ammonia capture from manure using gas-permeable membranes (closed loop).

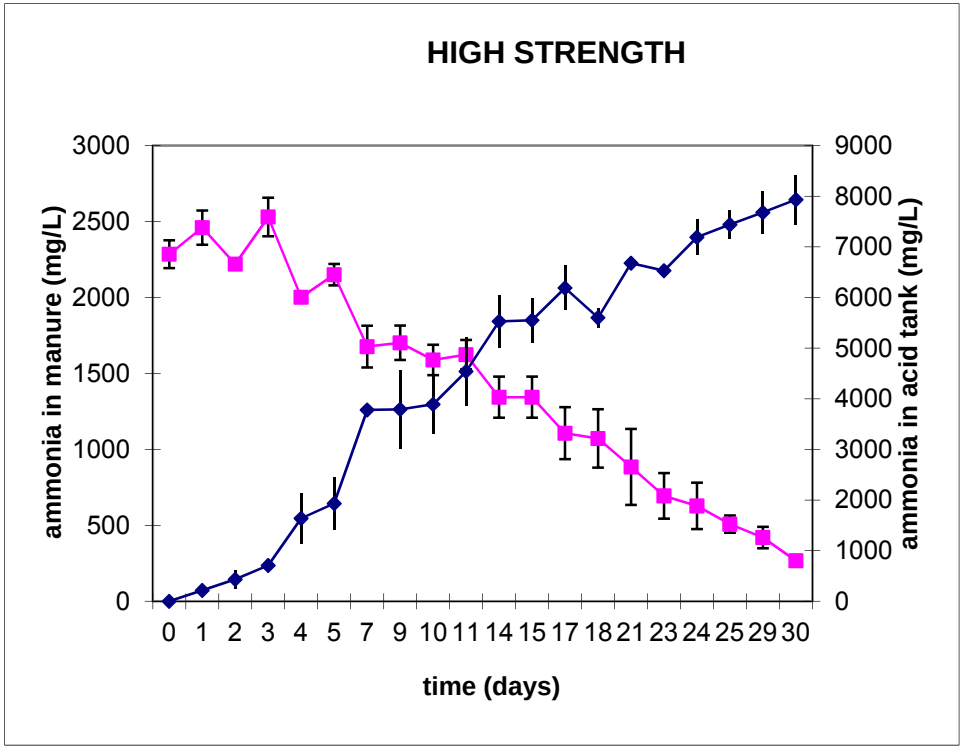


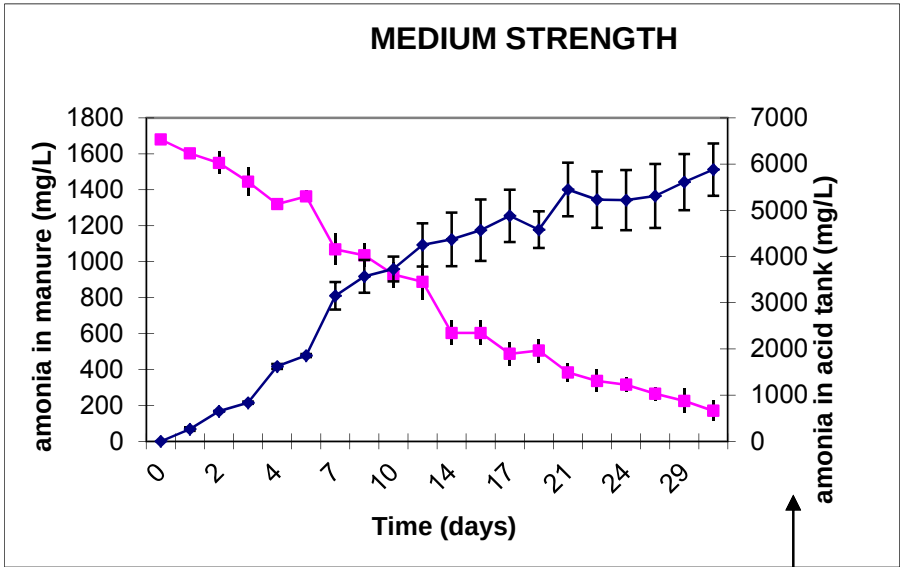
Process pH adjusted with alkali (7.7 to 9)



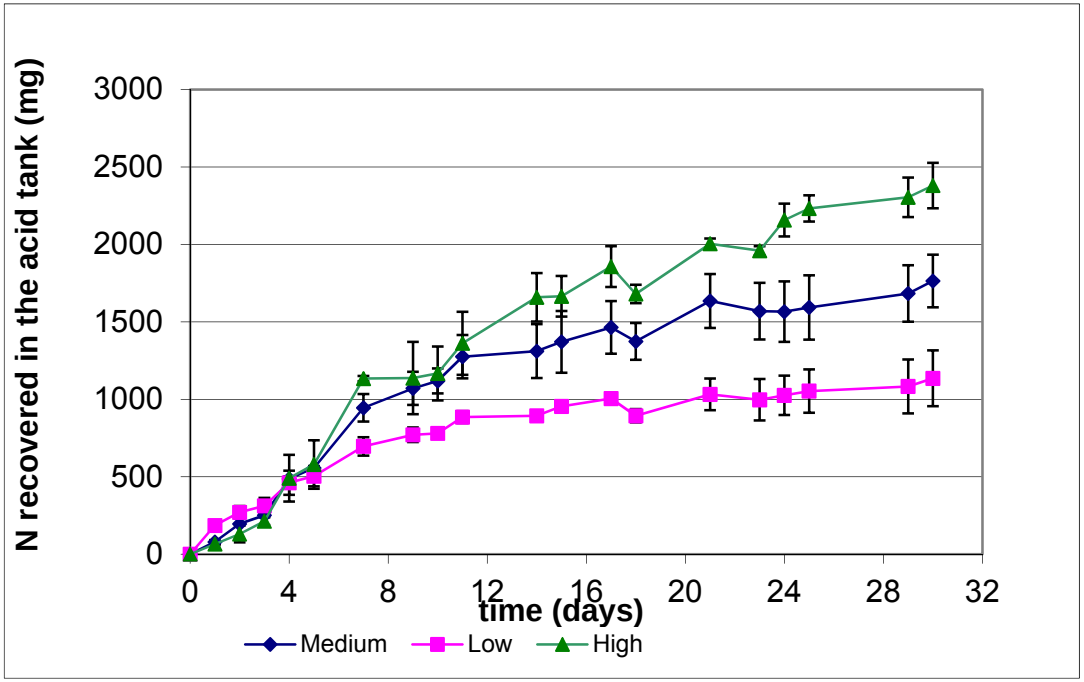
Removal of ammonia in the manures and recovery in the acid tank







Ammonia recovery rate increases with manure strength

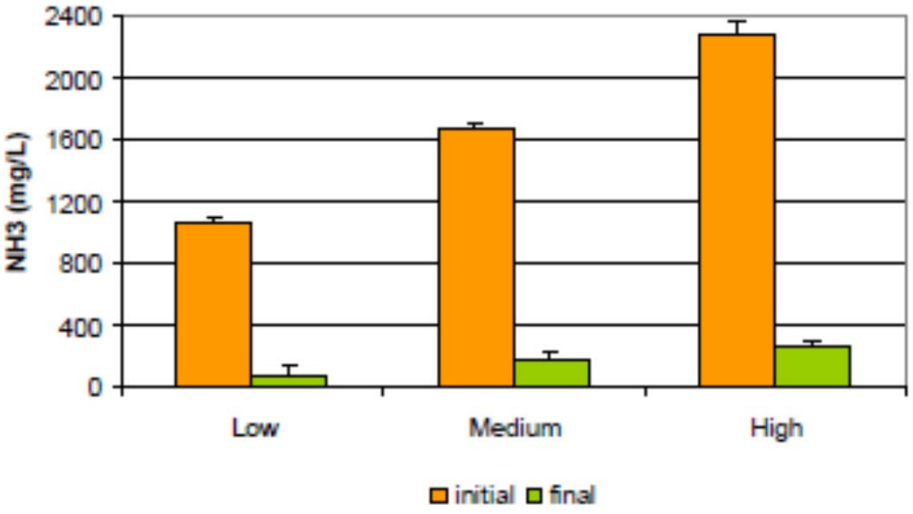


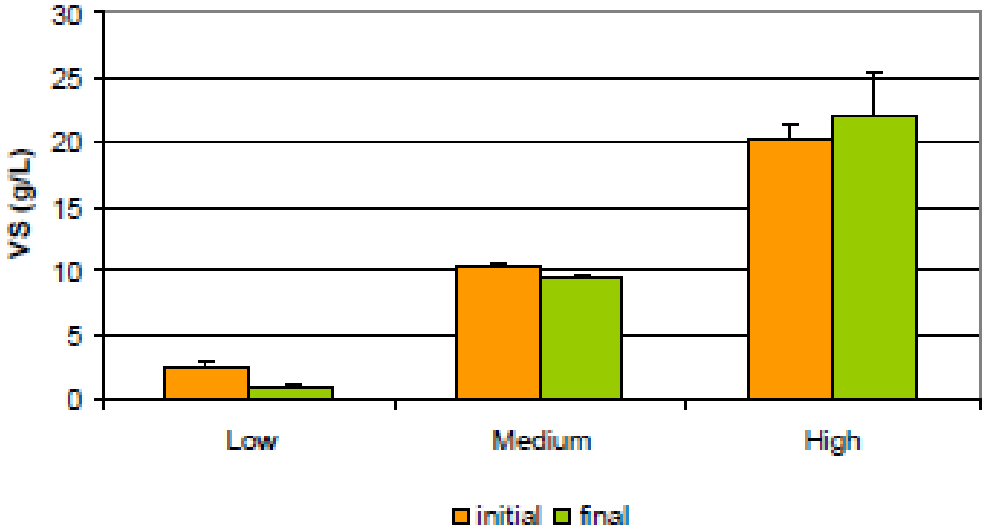
Manure strength	Initial NH4 mg N/L	NH4 removed %	NH4 recovery %	NH4 recovery rate (mg/L/d)
low	1385	94	87	74
medium	2184	90	90	92
high	2971	88	90	194

M.C. Garcia and M.B. Vanotti, Waste Management 2014 (in press)

Ammonia was removed

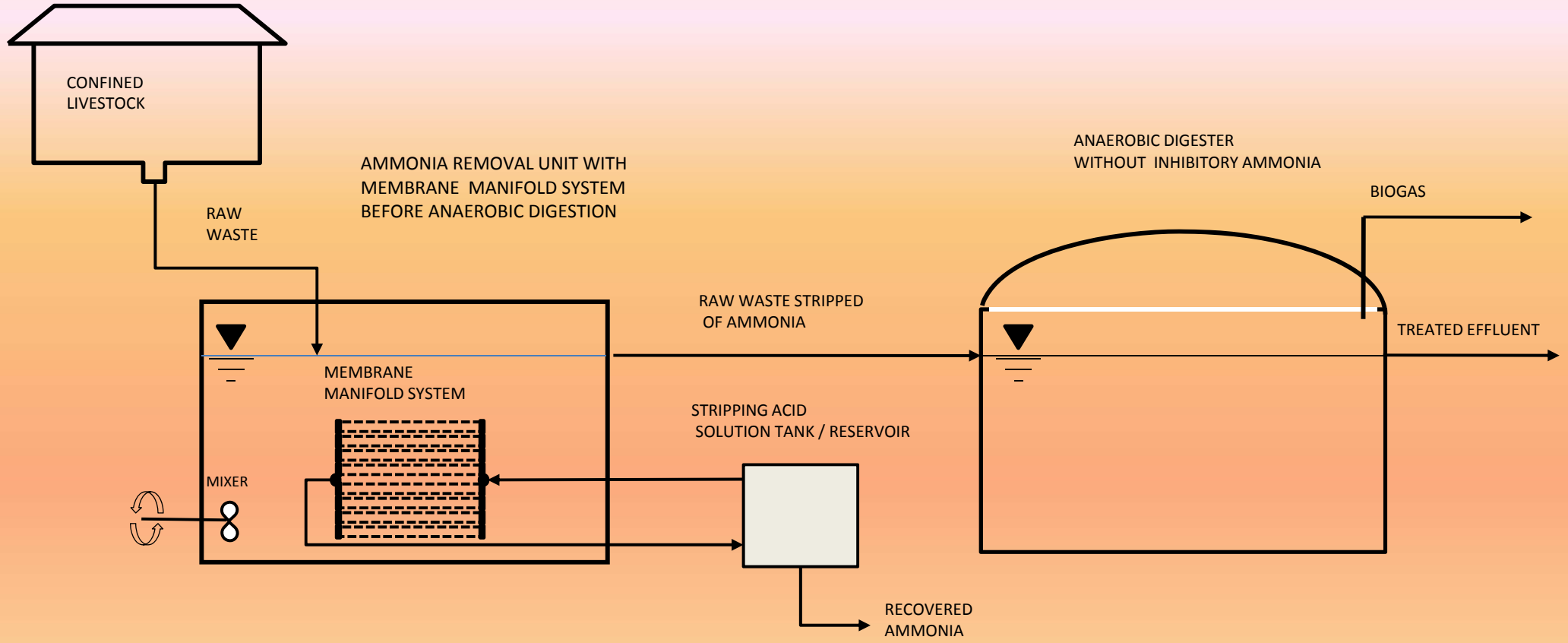
but carbon (volatile solids) was not removed





Technology can be combined with anaerobic digestion to recover both the ammonia and the energy from manure.

Ammonia Recovery System with Anaerobic Digestion



Design Parameter: Effect of aeration

Two ways can be used to increase manure pH and N recovery efficiency by the gas-permeable membrane system:

1. **Add alkali chemicals (OH^-)**

2. **Low-rate aeration**

$$HCO_3^- + air \rightarrow OH^- + CO_2$$
$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$

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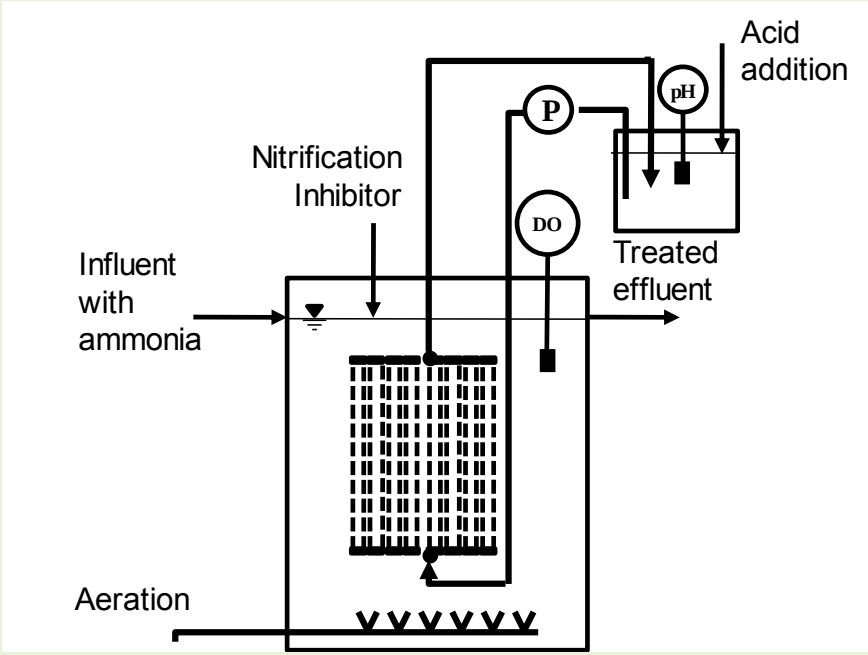
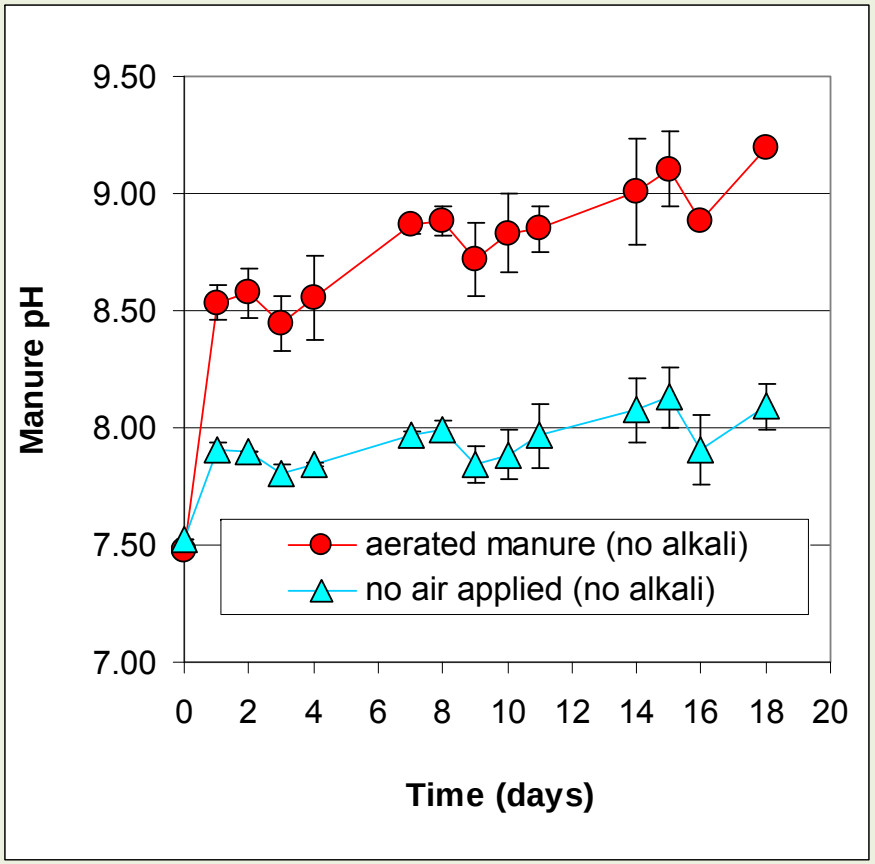


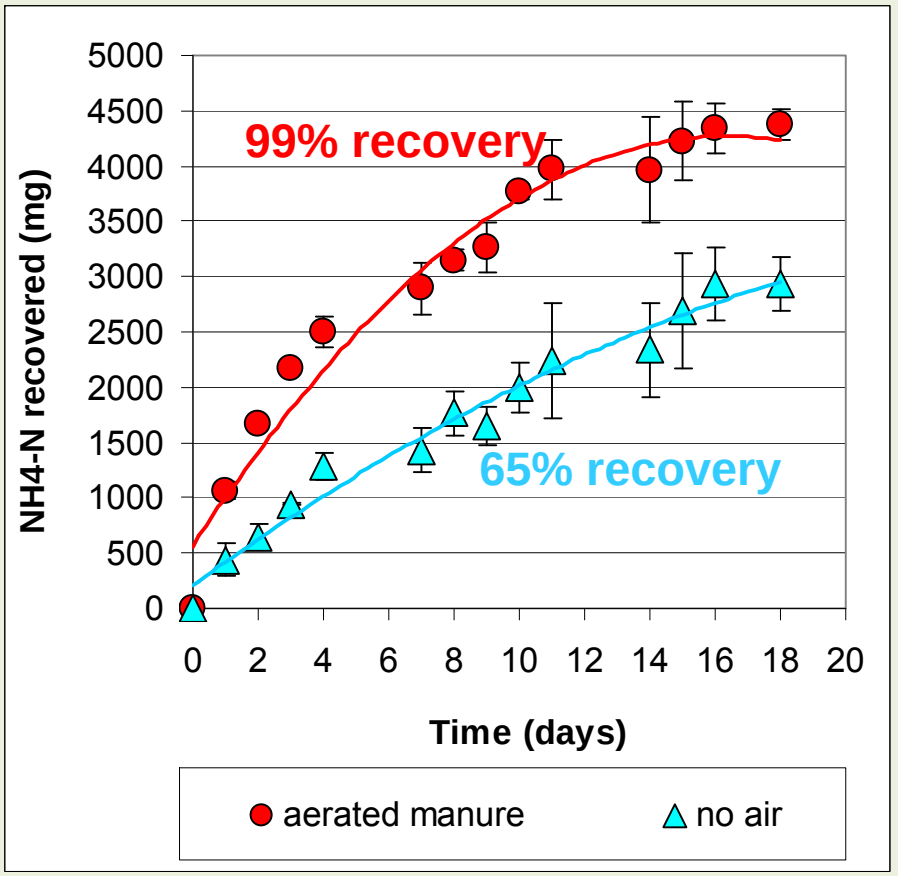
$$HCO_3^- + air \rightarrow OH^- + CO_2$$
$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$

- Aeration increases manure pH about 1 unit
- The aeration rate must be low to inhibit nitrification
- Nitrification inhibitor can be used (< 10 ppm)

Vanotti and Szogi. US 13/143,363 (2011)

Experiment with raw swine manure using gas-permeable membrane system with aeration and nitrification inhibition





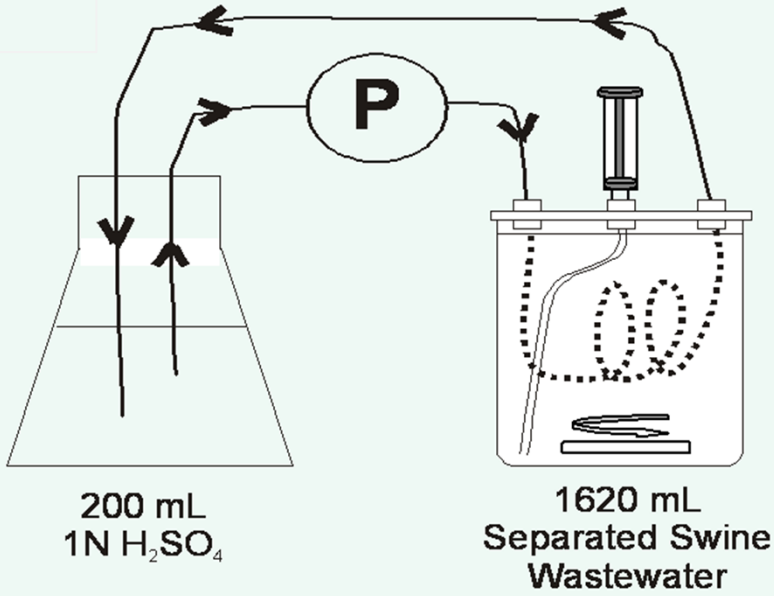
Aeration increased the pH of manure. As a result, the ammonia recovery by the membrane system was enhanced.

M.C. Garcia and M.B. Vanotti (2014).

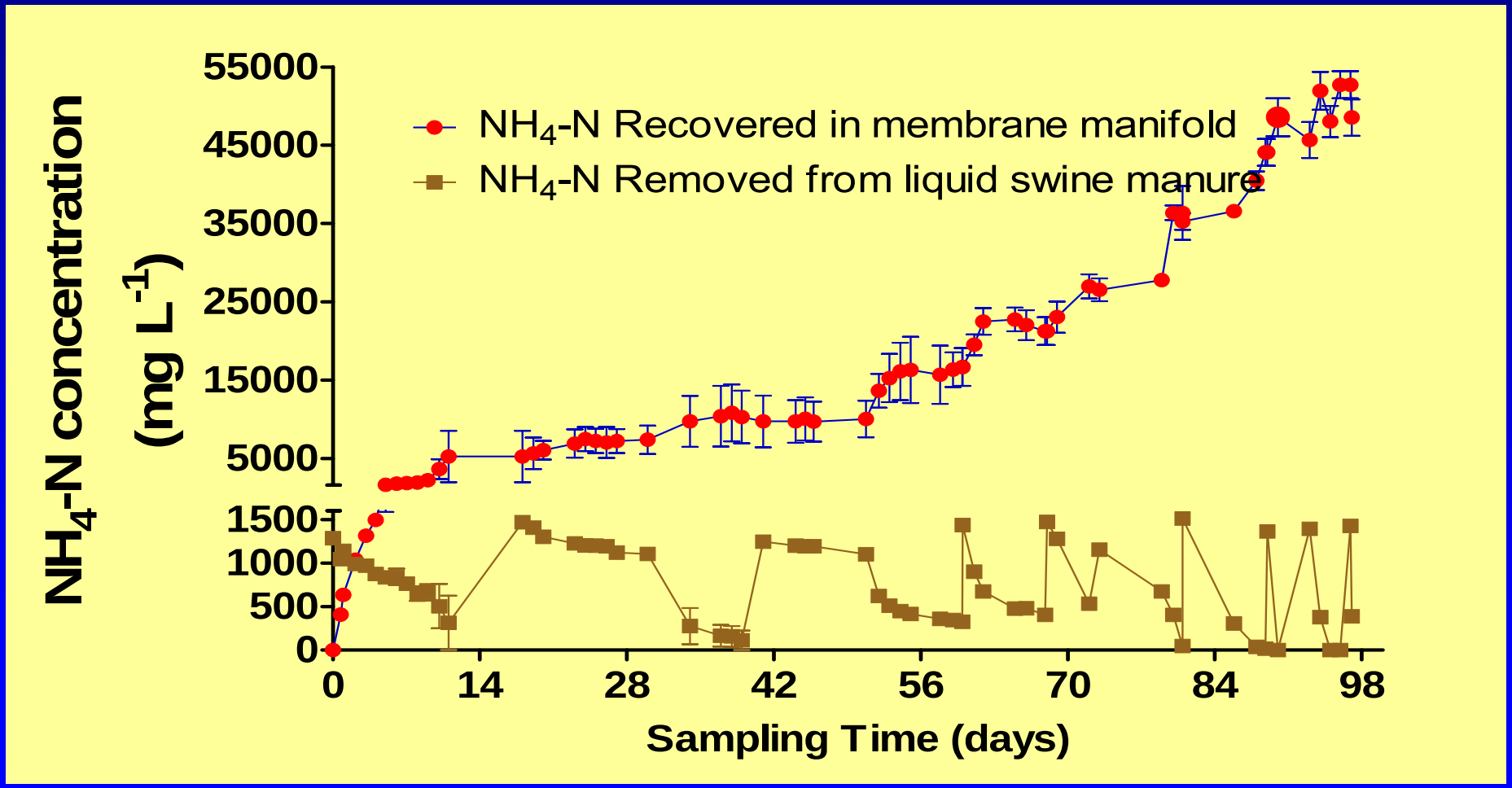
Design parameter: final concentration of the ammonia

Configuration	Wastewater	Strip solution	Effects studied
Closed recycle loop	Flushed Swine Manure NH_4-N = 1400 mg/L pH = 8.13 TS = 10,900 mg/L	1 N H_2SO_4	Repeated batches to concentrate N

Closed loop – Liquid manure

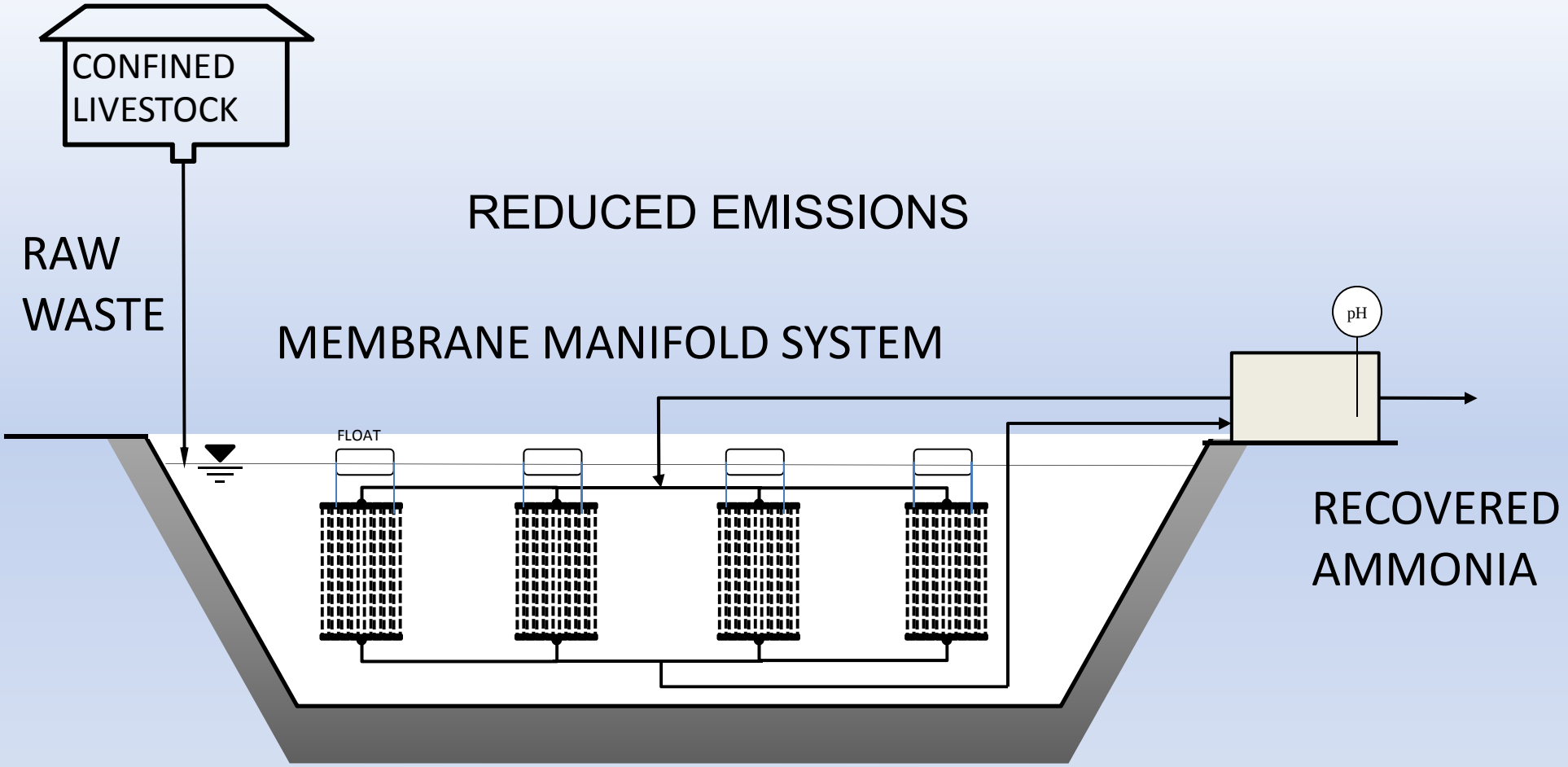


Recovery and Concentration of Ammonia from Liquid Swine Manure using Gas Membranes (10 batches using same stripping solution)



Recovered NH_4-N was concentrated to 53,000 ppm

Retrofit of manure storage units to harvest the ammonia

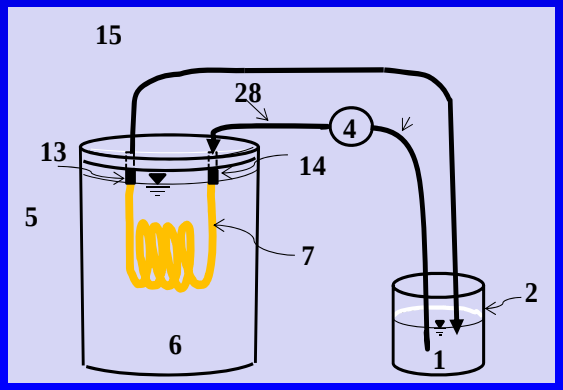


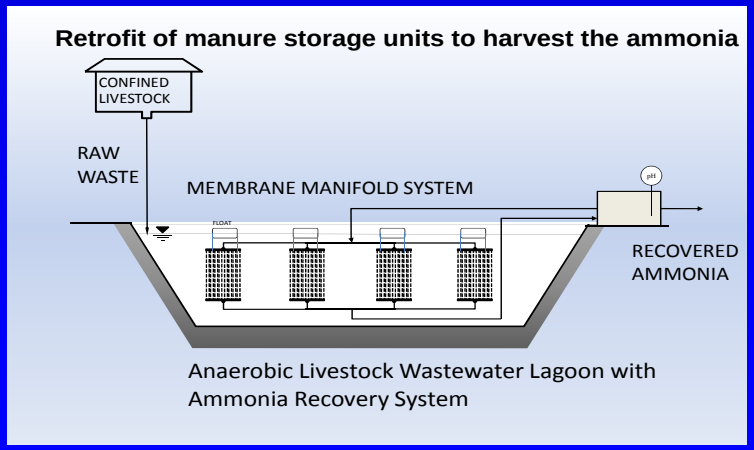
Anaerobic Livestock Wastewater Lagoon with Ammonia Recovery System

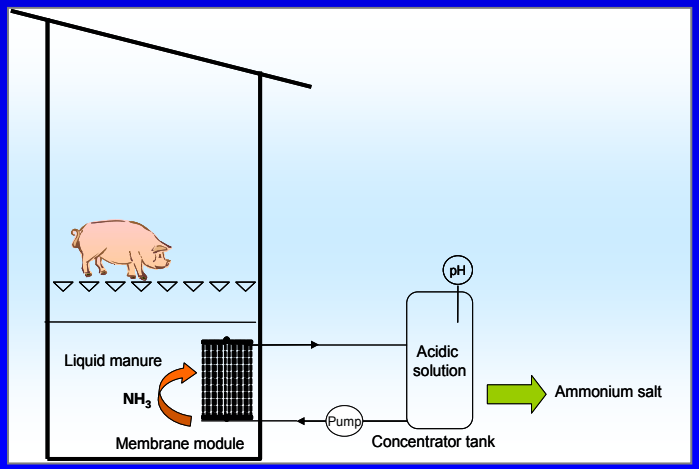
Recovery of Ammonia from Liquid Manure with Gas-permeable Membranes

- Technology captures ammonia emissions
- Produces liquid fertilizer with > 50,000 ppm nitrogen

- USDA Patent Appl. U.S. 13/143,363 (2011): "Systems and Methods for Reducing Ammonia Emissions form Liquid Effluents and for Recovering Ammonia".
- Commercialization/Licensing: USDA-ARS Office of Technology Transfer http://www.ars.usda.gov/business/business.htm







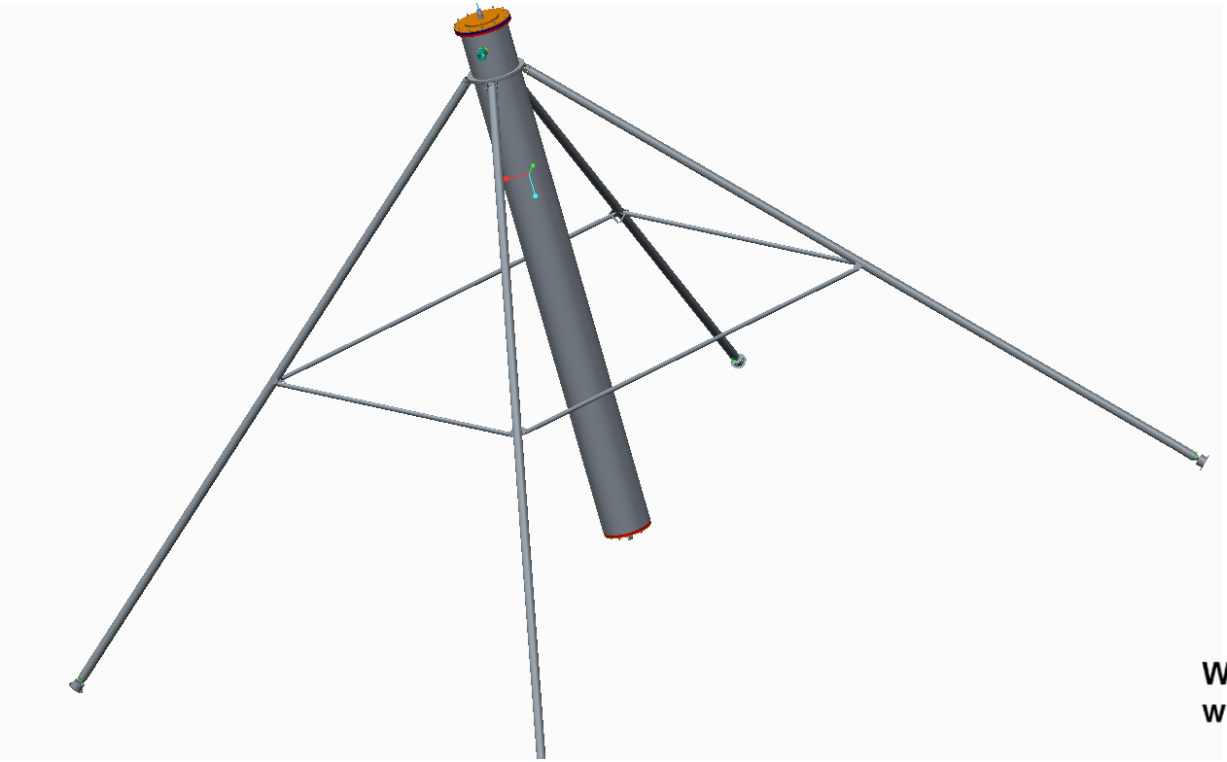
Ongoing research:

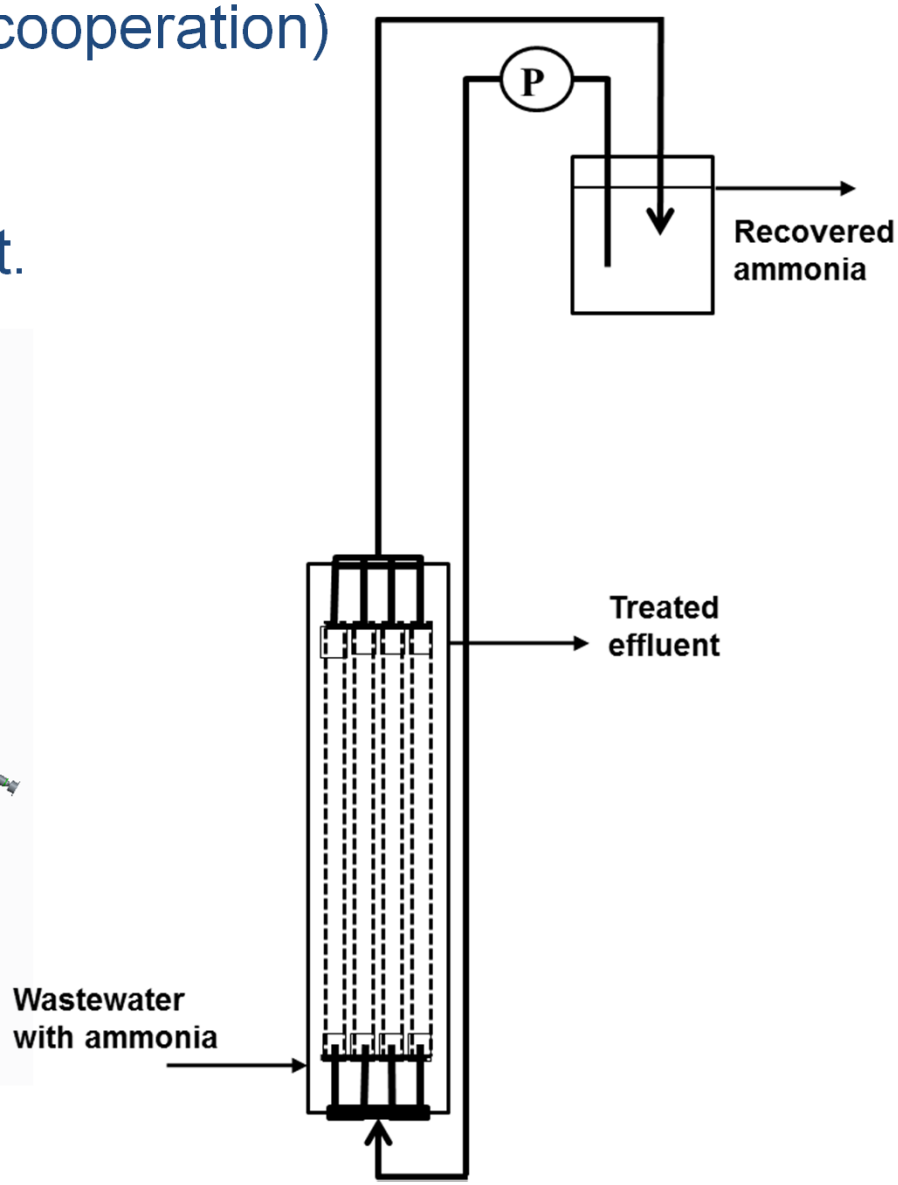
Grant from NRCS CIG (PI: Dr. John Classen, NC):

-Field demonstration (NCSU and ARS cooperation)

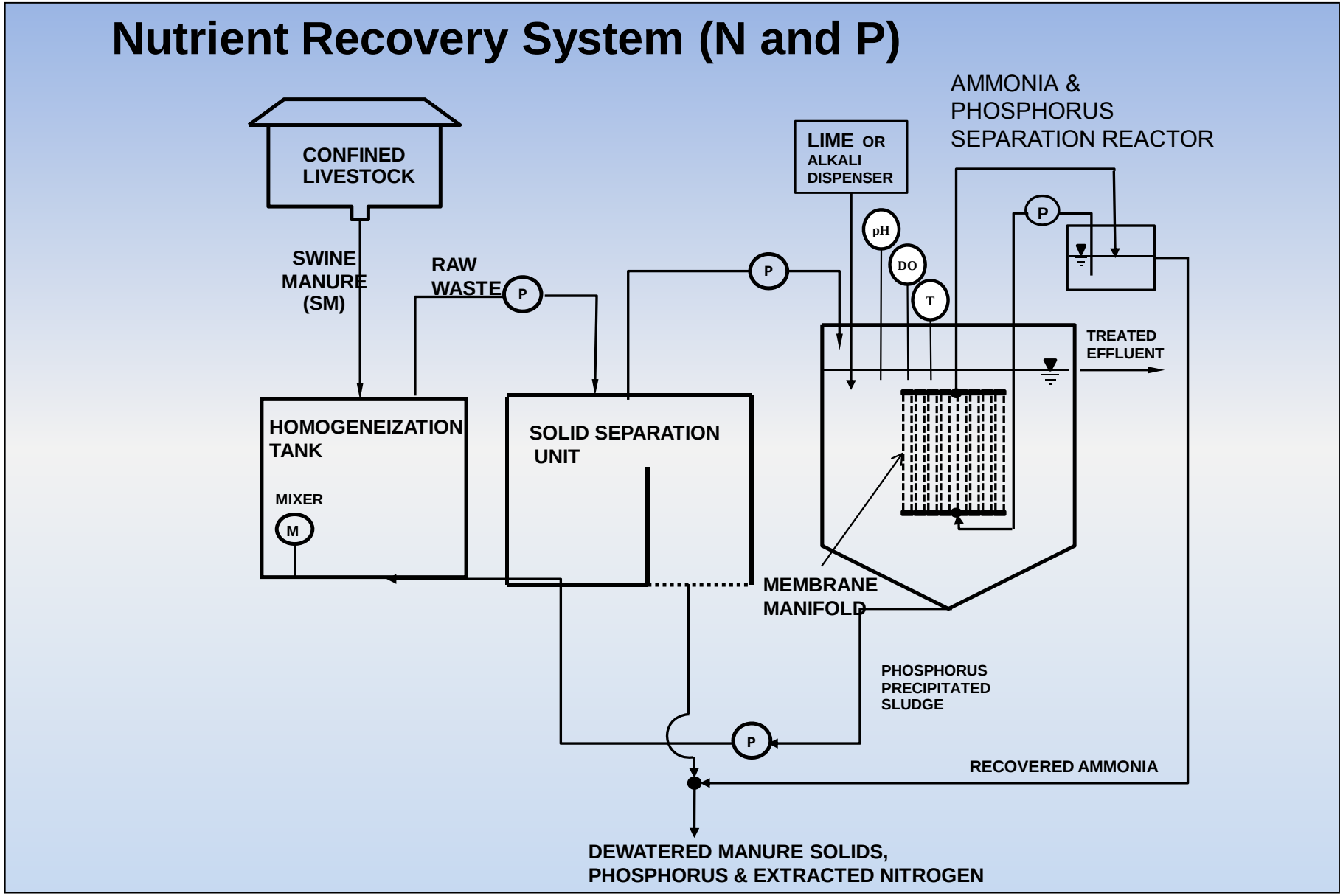
-Membrane pilot module being tested in 3 manure systems:

- anaerobic digester, scraper & belt.





Ongoing research: (ARS Florence, SC)

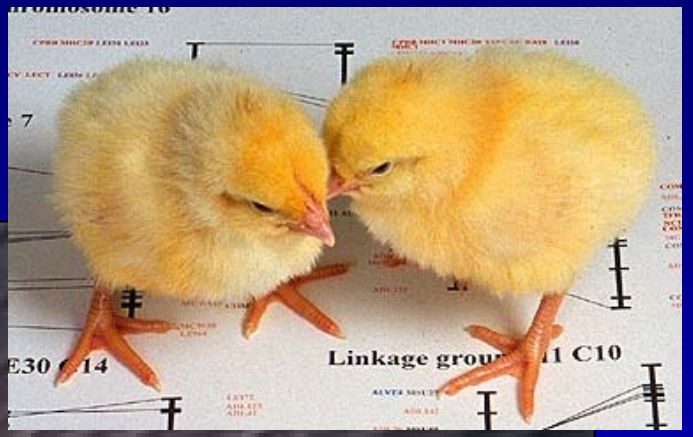


Presentation Outline:

1) **Ammonia Recovery from Liquid Manure**

2) **Ammonia Recovery from Air in Barns**

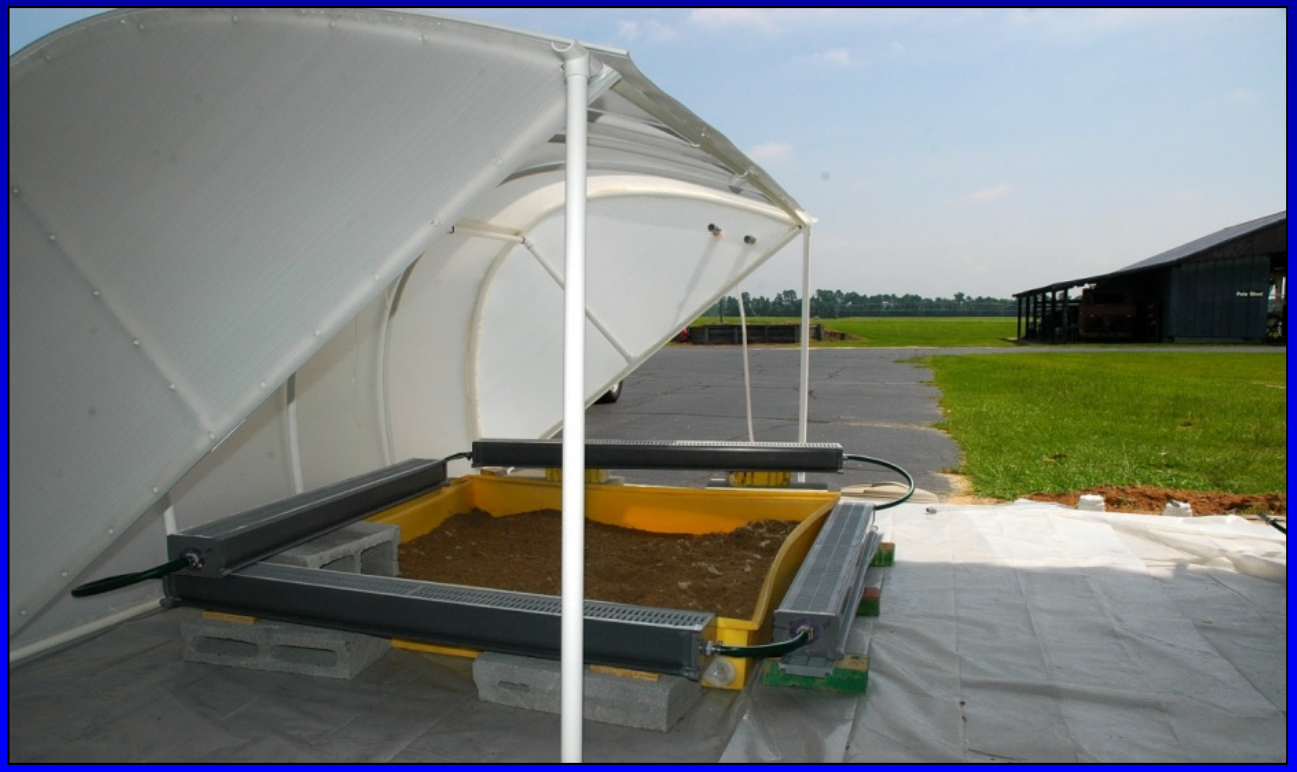
Broiler Production



AIR APPLICATIONS

Recovery of Ammonia from Poultry Litter using Gas-Permeable Membranes

Poultry Litter (Air)

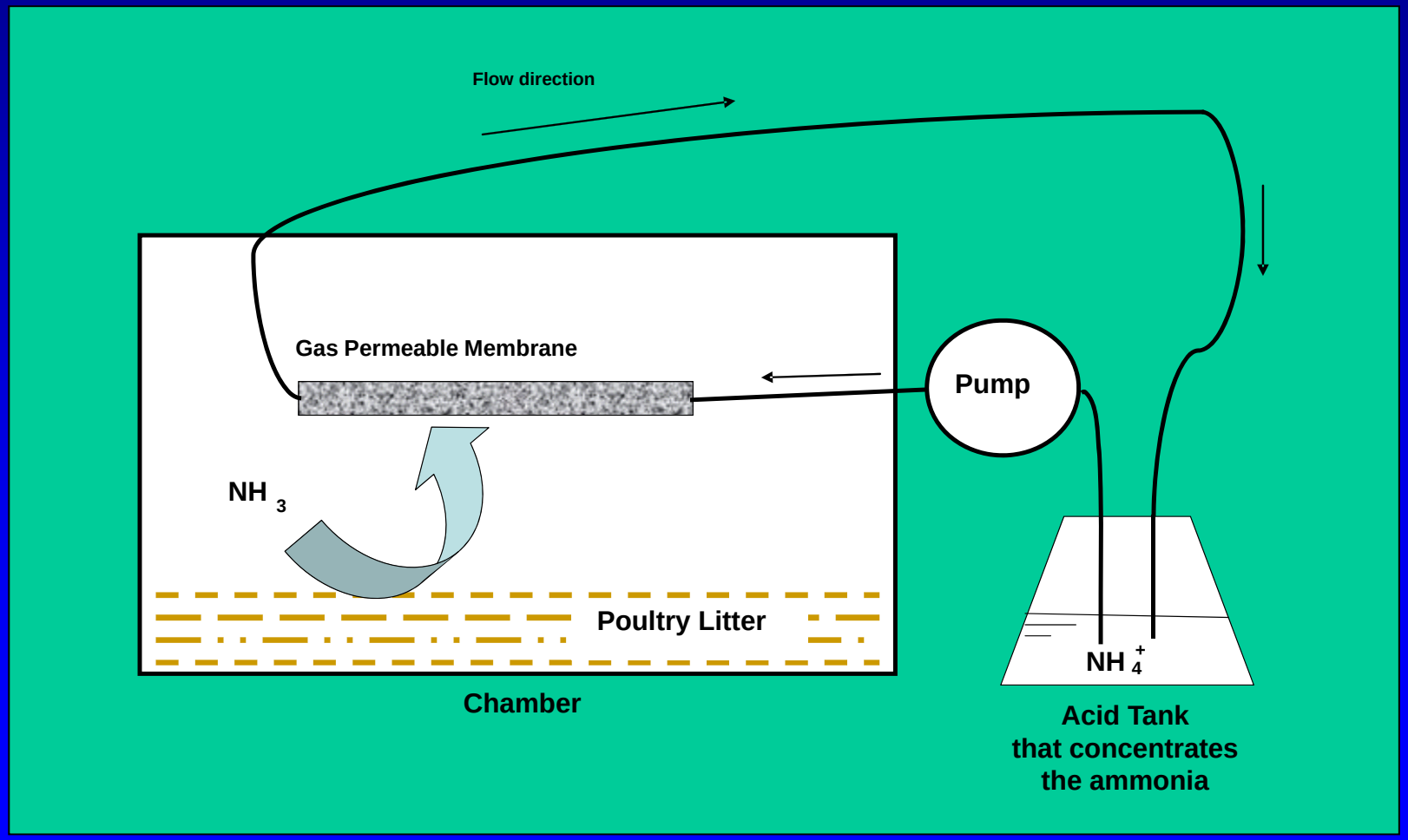


WHAT IS INTENDED TO DO?

- Removal near the NH_3 source, inside the poultry house. Cleaner air improves bird productivity.
- No need of intense air ventilation, which reduces heat loss from poultry house.
- Nitrogen is recovered in a concentrated, purified form

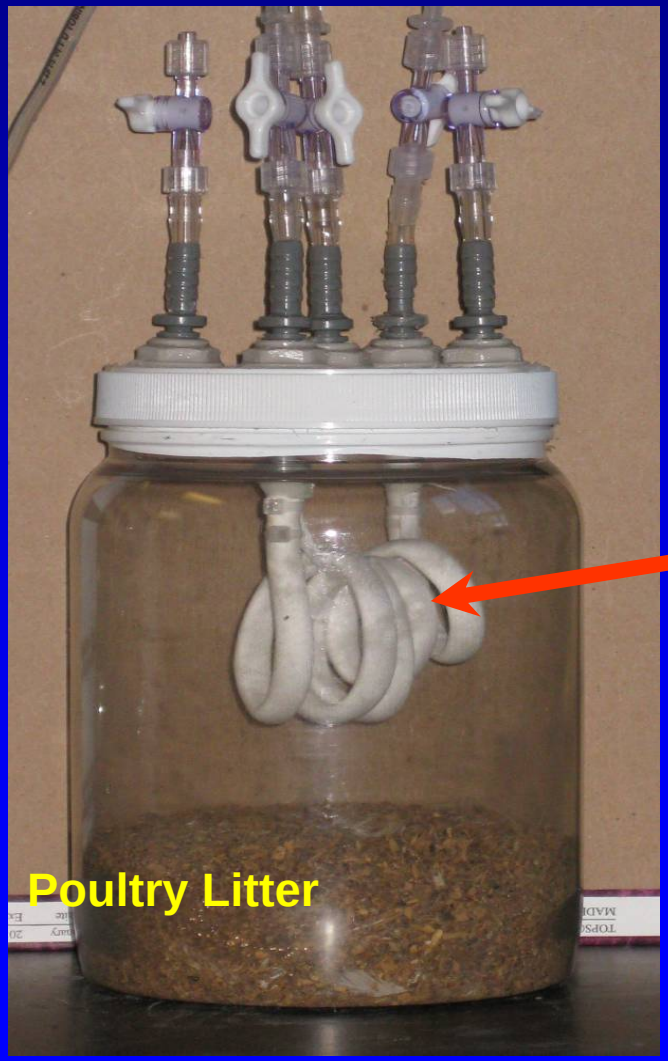
How does it work?

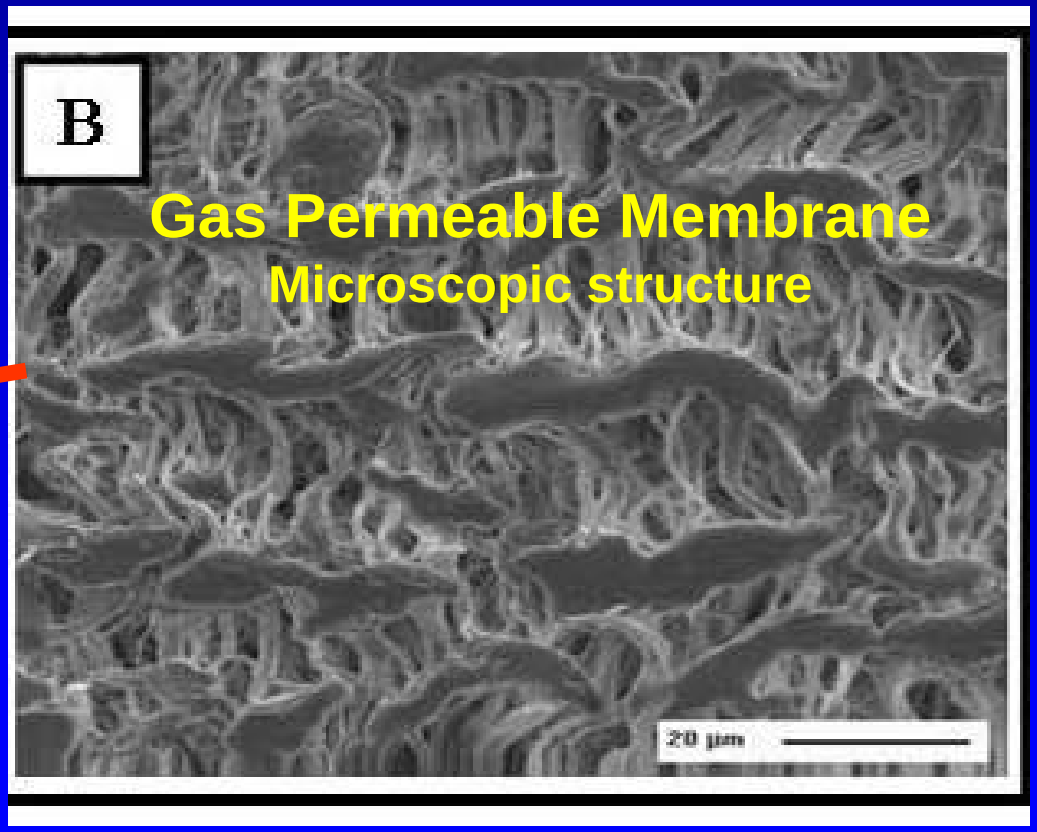
Removal of NH_3 from Air Using Tubular Membranes



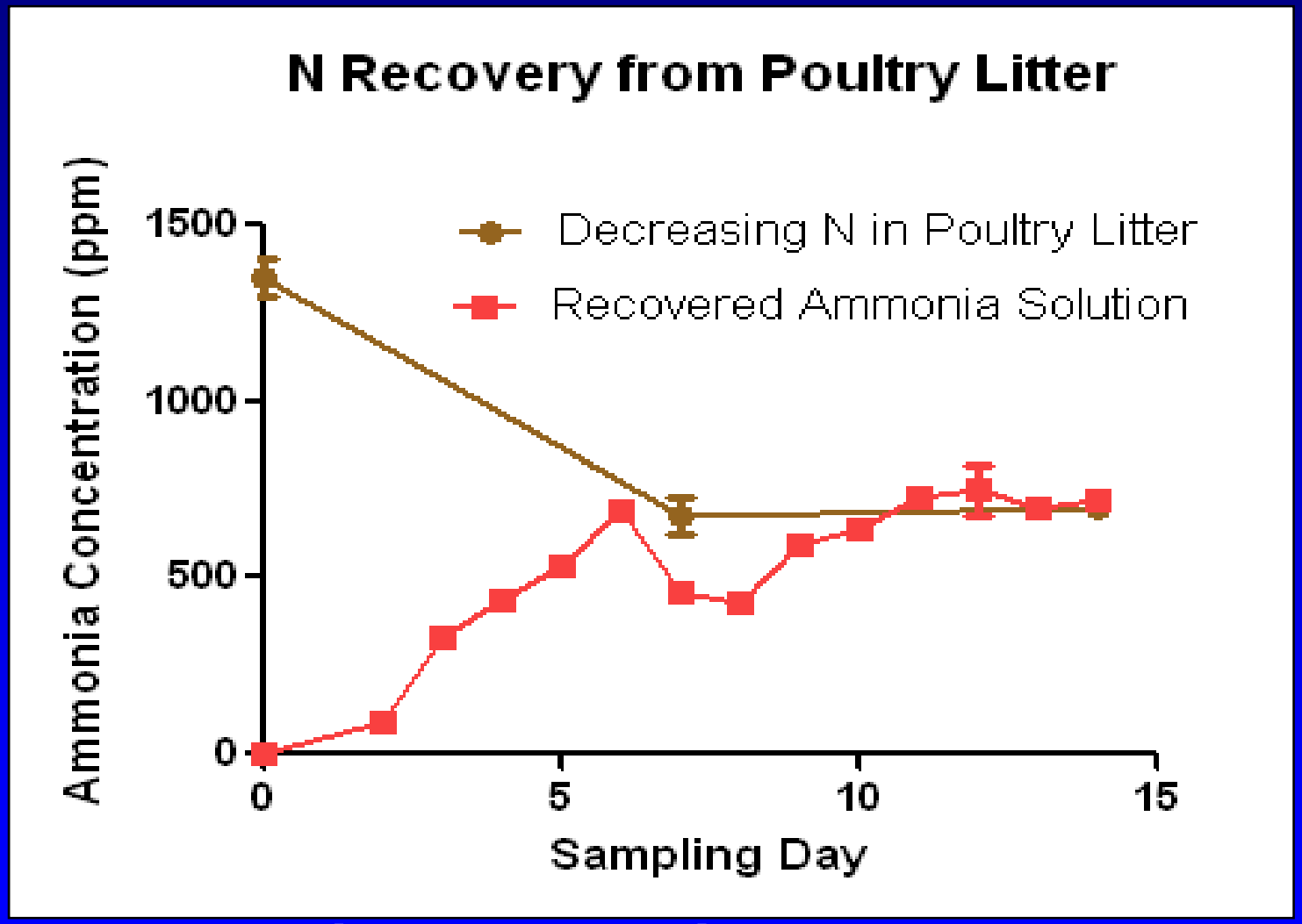
TUBULAR MEMBRANES

Removal of NH_3 from Air Using Gas-Permeable Membranes





Removal of NH_3 from Air Using Tubular Gas-Permeable Membranes



Simple Experiments

Mass balance showed quantitative recovery

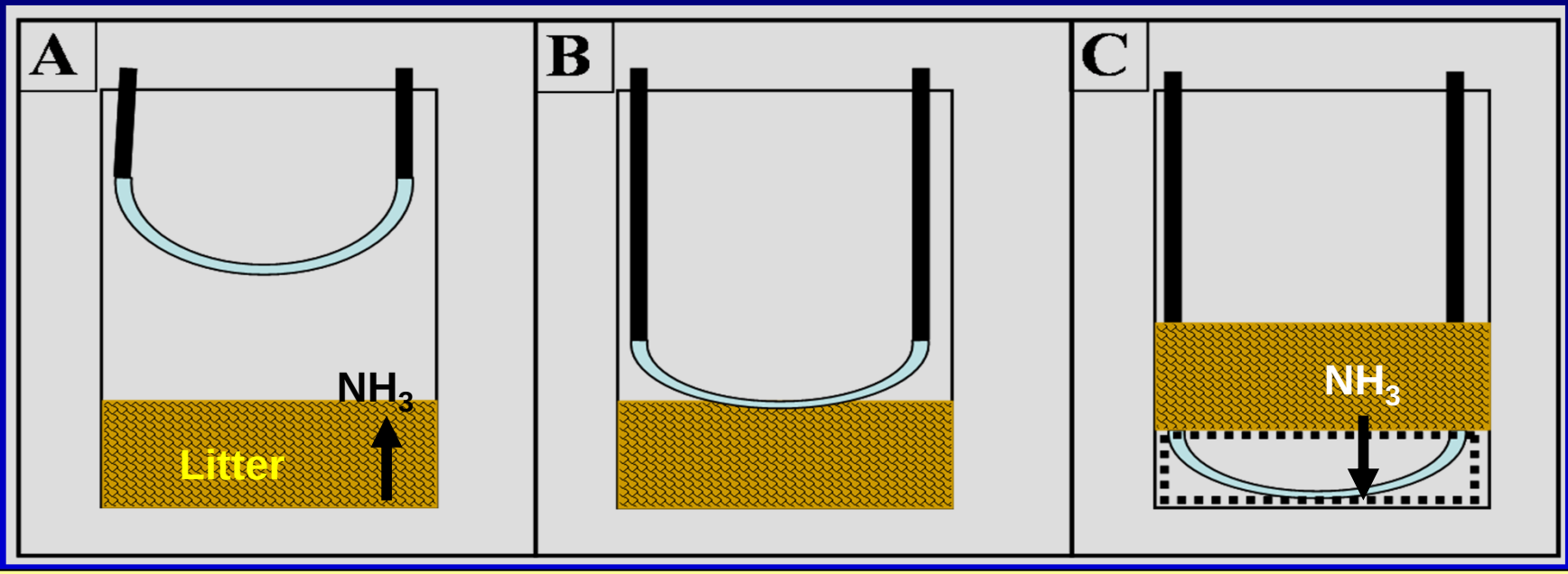
Weekly mass balance and percent recovery of NH_3 from poultry litter with ePTFE tubular membranes

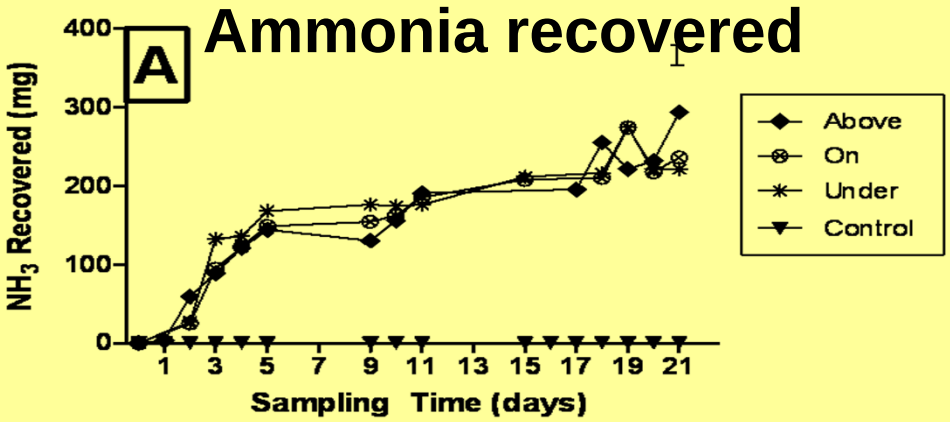
Sampling Time (days)	NH_4-N Content of Litter (mg kg^{-1})	NH_4-N Mass Loss from Litter (mg)[b]	NH_4-N Mass Recovered in Acid Trap (mg)	NH_4-N Recovery (%)
0	1369.2 (9.2)	0	0	0
7	758.3 (8.2)	211.4 (4.1)	172.3 (3.3)	81.5
14	766.7 (9.9)	208.4 (6.1)	199.7 (3.7)	95.8
21	791.7 (7.2)	207.3 (4.0)	230.0 (3.6)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

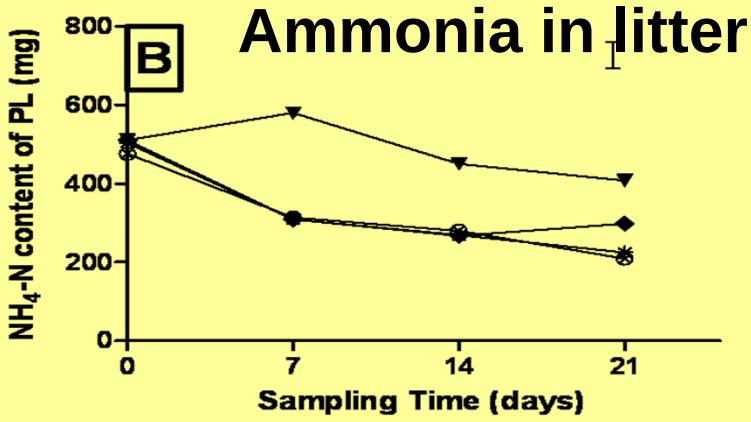
Design Parameters

- Position in the barn
- Timing: Time available for recovery
- Tubular or flat membranes

Position of Tubular Membrane: equally effective







Rothrock, Szogi & Vanotti. 2010. Recovery of ammonia from poultry litter using gas-permeable membranes. Trans. ASABE 53:1267-1275.

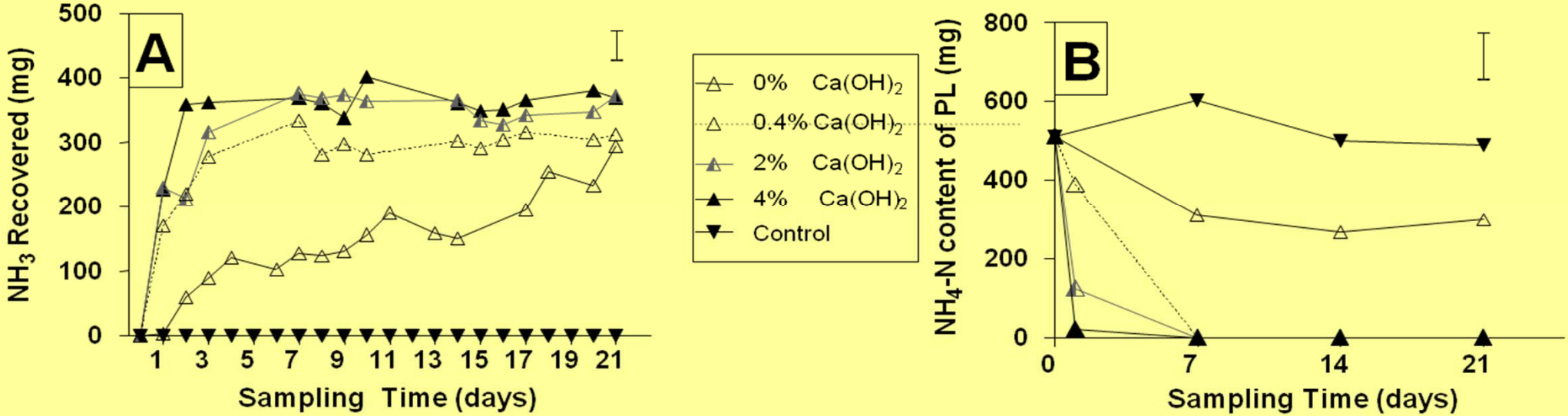
Membrane modules: possible placement

- Close to litter surface (reduced NH_3 exposure to birds).
- Suspended above litter (like bird feeders and drinking devices).
- Retrofitted on the walls of the building.
- Below the poultry litter bed or cages.

TECHNOLOGY HAS IMPLICATIONS IN THE FUTURE DESIGN OF ANIMAL HOUSING

Timing:

Accelerated Recovery of NH_3 with Hydrated Lime



Producers choosing <u>to disinfect</u> the poultry manure using lime could benefit from this membrane system by recovering the NH_3 rapidly released from the litter upon lime application.

Ammonia concentration in the air was substantially reduced using gas-permeable membrane manifold

NH_3 concentrations from poultry litter seven days after lime addition of hydrated lime

Hydrated Lime Added to Poultry Litter (% w/v)	NH_4-N Mass Loss from Litter (mg)	NH_3 Headspace Concentration without Membrane (mg L^{-1})	NH_3 Headspace Concentration with Membrane (mg L^{-1})
0	202	8.8	0.2
0.4	511	34.0	0.0
2	511	17.8	0.0
4	511	14.6	0.0
$LSD_{0.05}$	14	7.2	0.02

FLAT MEMBRANES

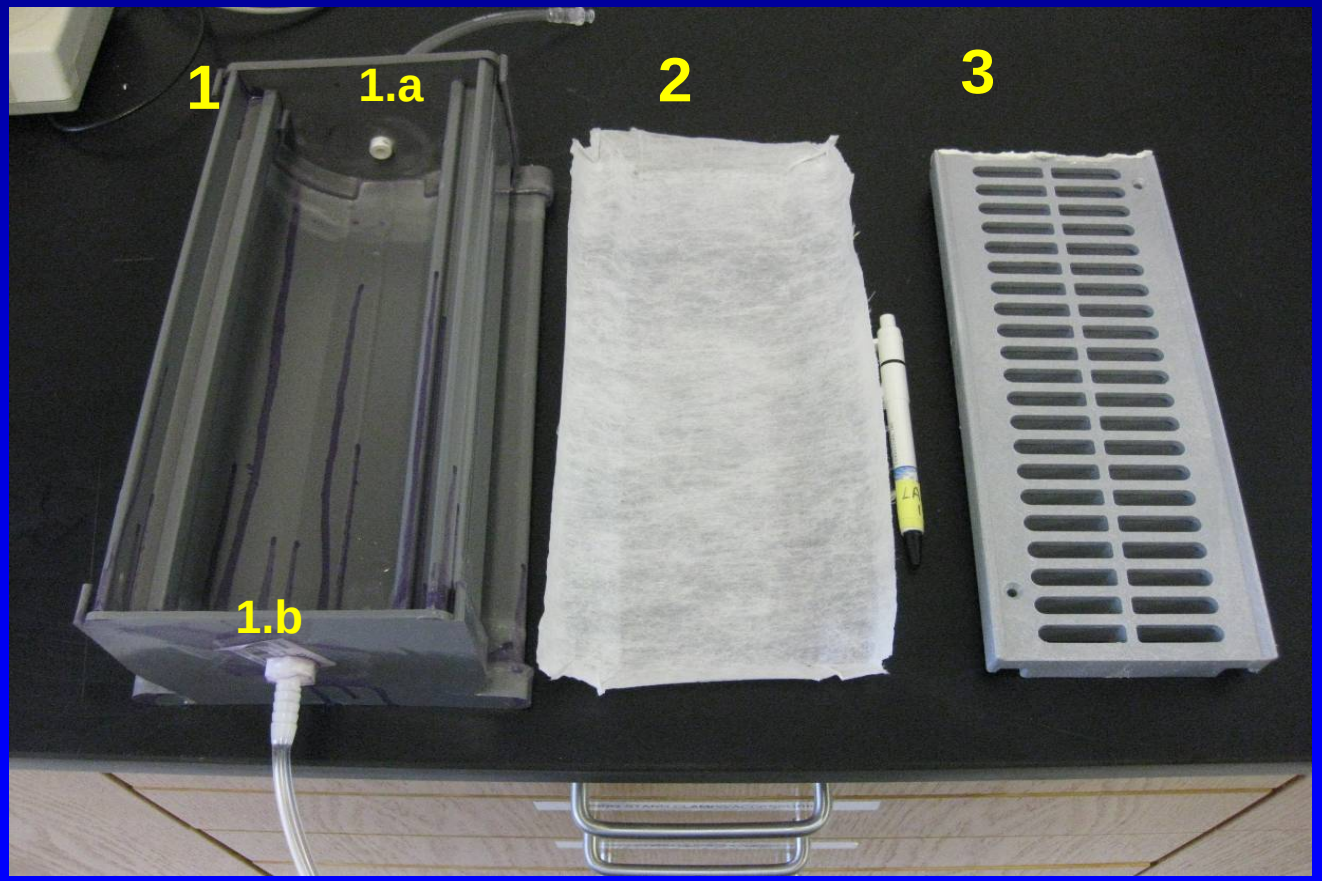
fitted to a PVC drain channel

MANIFOLD

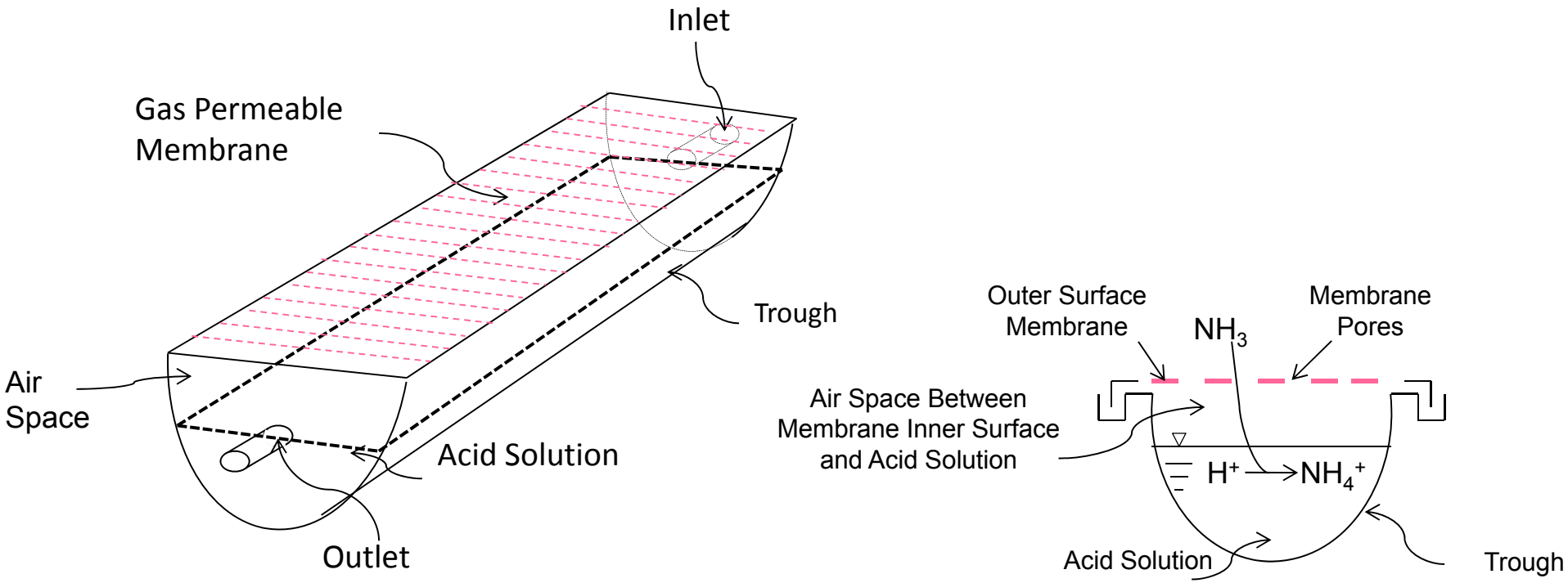
1. PVC Channel
1.a Inlet
1.b Oulet

2. EPTFE Permeable Membrane

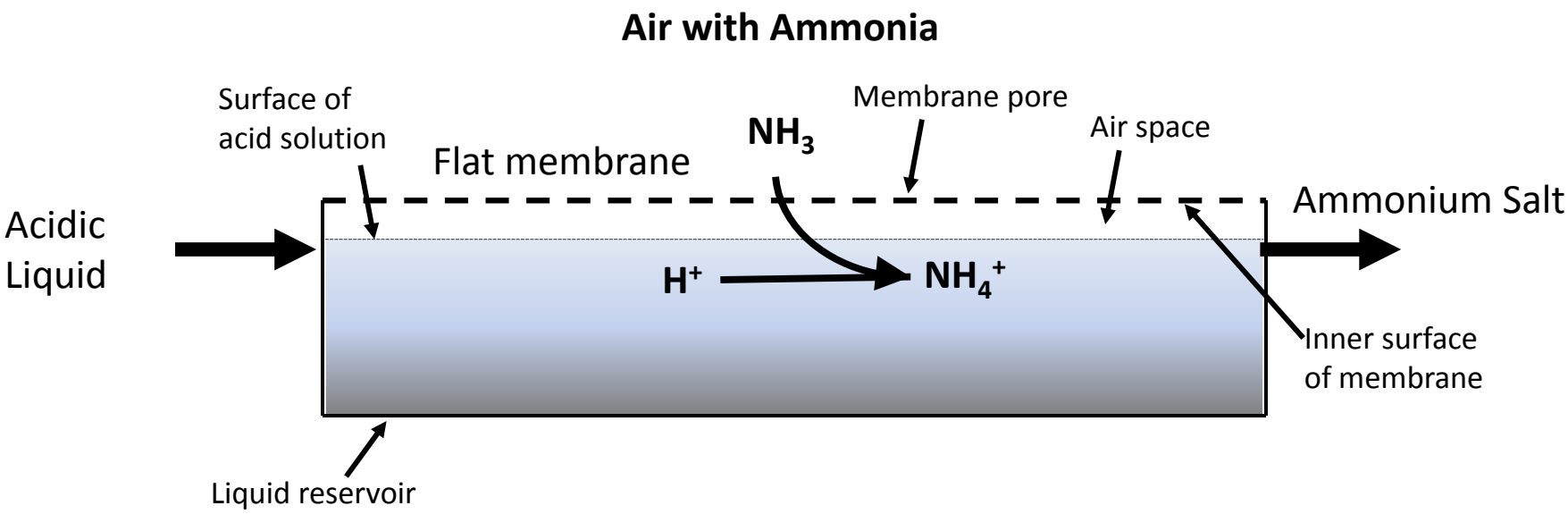
3. Lid



Flat Gas Membrane Device

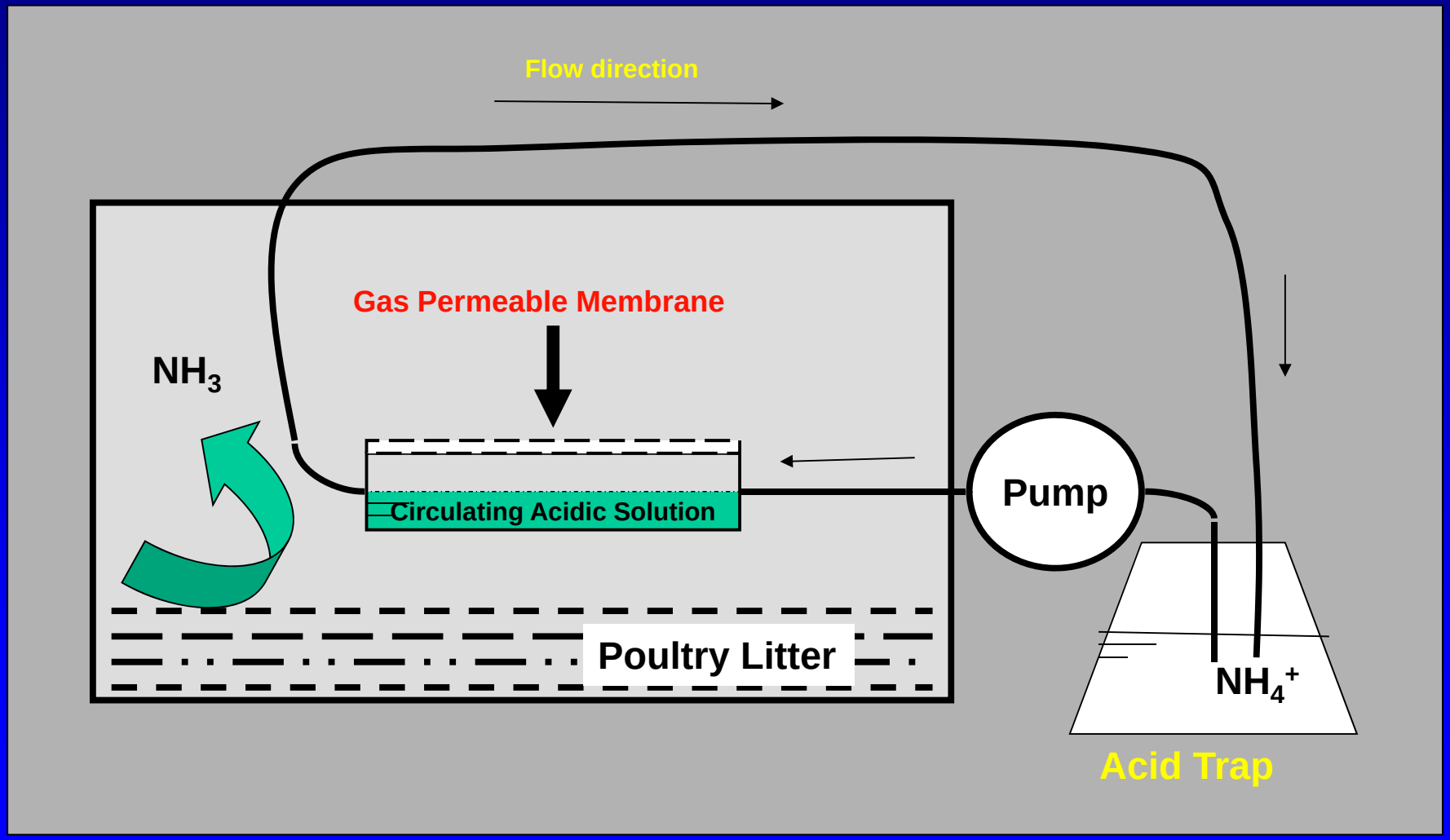


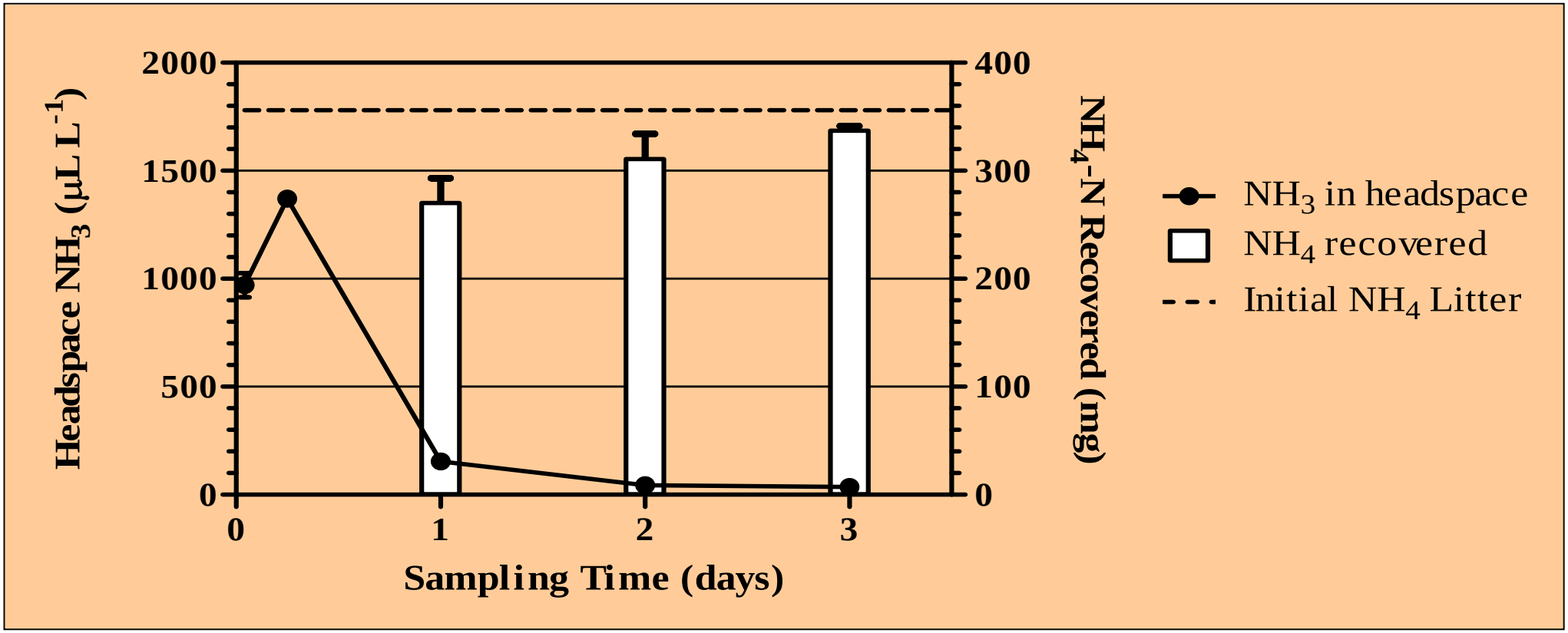
FLAT MEMBRANES



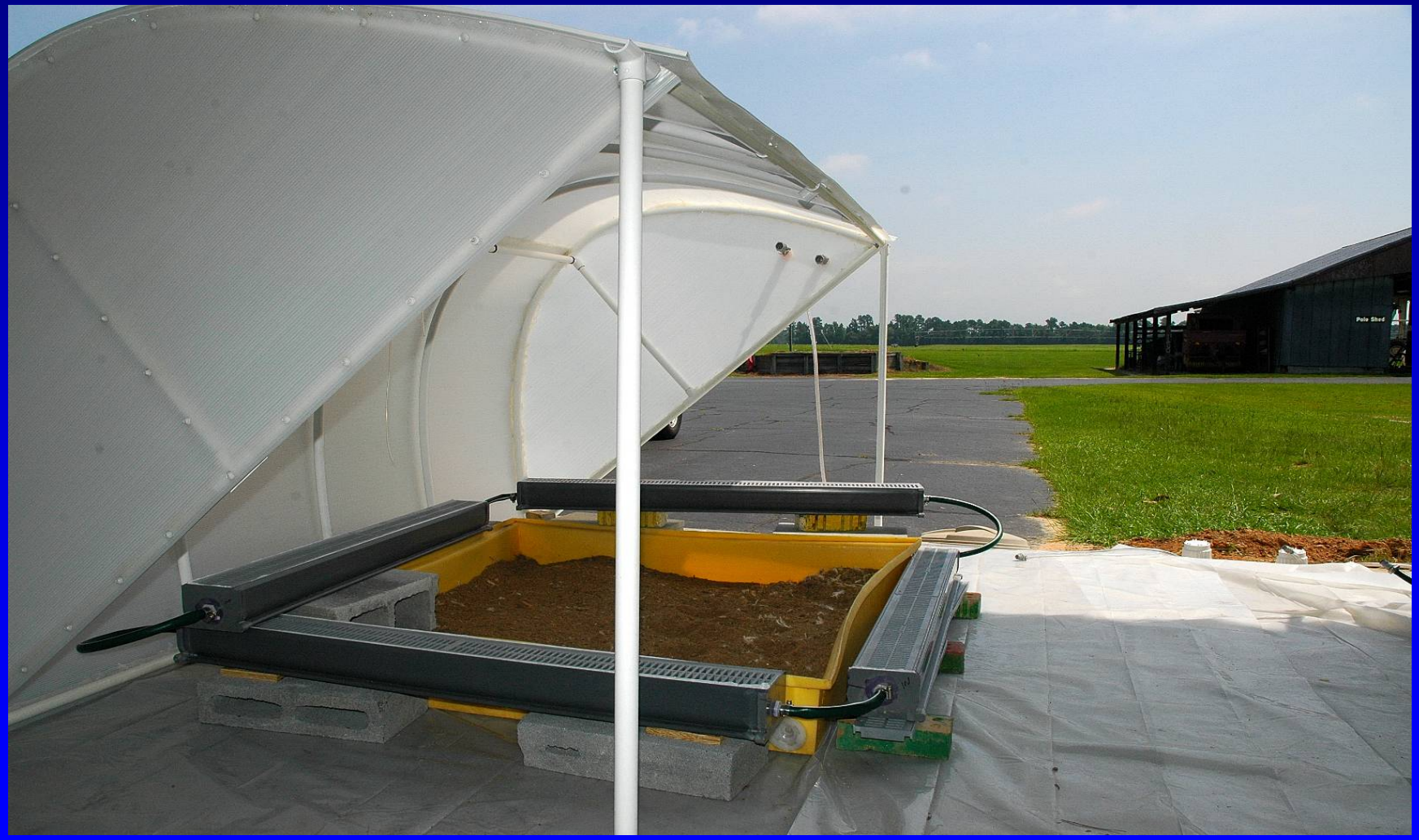
FLAT MEMBRANES

Removal of NH_3 from Air Using Gas-Permeable Membranes – Concept Prototype




2000
1500
1000
500
0
400
300
200
100
0
0
1
2
3
Headspace NH3 (µL L-1)
NH4-N Recovered (mg)
Sampling Time (days)
NH3 in headspace
NH4 recovered
Initial NH4 Litter

Pilot Field Experiment
Poultry Litter - ARS Florence, SC

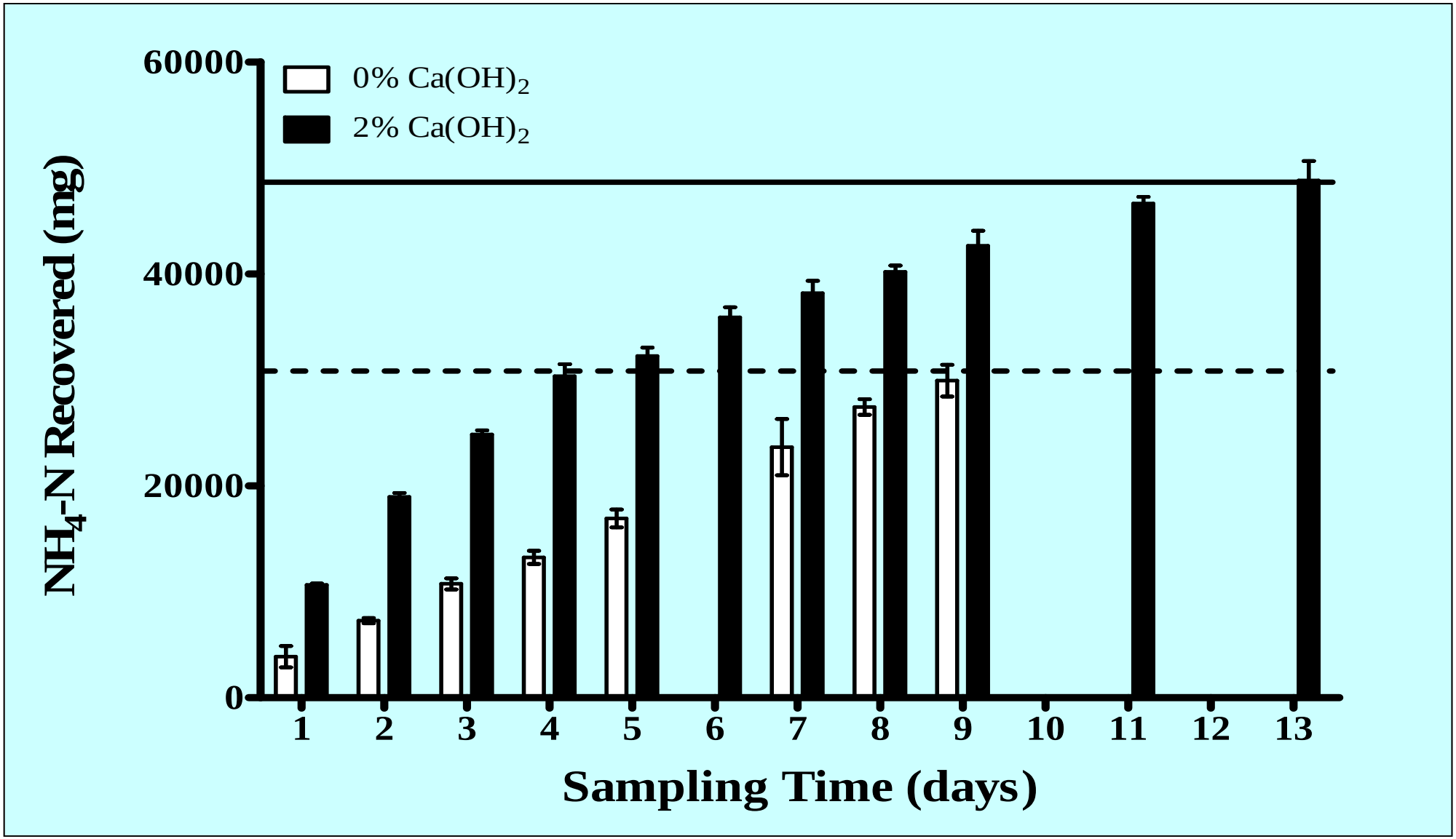


Recovery of ammonia using a field-scale flat membrane manifold system under normal and enhanced volatilization conditions[a][b]

Mass balance showed quantitative recovery

$Ca(OH)_2$ ($w\ v^{-1}$)	Initial NH_3 in Litter[c]	Final NH_3 in Litter[c]	NH_3 Lost from Litter[d]	NH_3 Recovered in the Acid Solution	NH_3 Recovery[e]
%	----------mg----------				%
0	139236	108590	30646	29942	97.7
2	48427	0	48427	48830	100.8
		p value	0.0012	<0.0001	0.8983

[a] 32.5 kg litter in a 2.51 m^3 enclosure using 13.5 L 1N H_2SO_4 (recirculation rate = 27 L hr^{-1})
[b] Days of experiment: 0% = 8.76 days; 2% = 12.73 days
[c] Measured using 2M KCl extraction method and colorimetry using an autoanalyzer (Peters et al., 2003)
[d] Peak gaseous NH3 concentration in air: 0% = 915 µL L-1; 2% = >2000 µL L-1
[e] NH_3 Recovery = (NH_3 Recovered in Acid/NH_3 Lost from Litter) * 100


60000
40000
20000
0
0% Ca(OH)2
2% Ca(OH)2
NH4-N Recovered (mg)
1
2
3
4
5
6
7
8
9
10
11
12
13
Sampling Time (days)

Recovery of Ammonia Removal from Air in Poultry Houses

- Gas membrane technology captures 97% of the ammonia near the litter
- Reduced ammonia inside the house benefits bird health
- Produces a liquid fertilizer
- USDA Patent U.S. 13/048,375 (2011)

On going research:

Grant from USDA NIFA's 1890 Capacity Building Program Univ. Maryland Eastern Shore (UMES) – Dr. Fawzy H. Hashem (PI)
Cooperation of ARS (Beltsville & Florence) with UMES

- **Testing Capacity of Ammonia Removal from Air in Poultry Houses**
- **Project integrating poultry house heating, nitrogen recovery with gas membranes and bio-fertilizer production (Chesapeake Bay site)**

On going research:

Grant from USDA NIFA's 1890 Capacity Building Program Cooperation of ARS (Beltsville & Florence) with UMES, Dr. Pat Millner (Beltsville)

- Testing Capacity of Ammonia Removal from Air in Enclosed Composters

http://www.ars.usda.gov/saa/cpswprc