Recovery of Phosphate and Ammonia from Animal Waste: A New Paradigm in Agriculture

ReUseWaste Kick Off Meeting
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Matias Vanotti

USDA-ARS Coastal Plains Research Center
Florence, South Carolina, USA
Estimated distribution of industrially produced pig populations

Source: LEAD.
Concentration of pig production in USA
North Carolina produces approximately 750 million chickens, 40 million turkeys, 3.5 billion table eggs, and 19 million hogs per year.
Percent of Agronomic Crop and Forage Phosphorus Needs Supplied by Recoverable Plant Available Manure Phosphorus at the County Level in North Carolina

Source: Barker & Zublena
Global Fertilizer Prices

Source: IFDC
Escalating U.S. Fertilizer Costs

Energy and Agriculture

Fertilizers 28%
Diesel 27%
Electricity 21%

Yearly Costs:
- Potash
- Anhydrous nitrogen

Cost per ton ($):
- 2010
- 2000
- 1990
- 1980
- 1970
- 1960
- 1950

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Presentation outline: **Nutrient recovery technologies at USDA-ARS**

- Soluble P extraction after buffer removal
- Solids-liquid separation with polymers
- Quick wash P recovery from solid manures
- Biochar P fertilizer
- N recovery with membranes
Recovery of Phosphate from Wastewater

On-farm Phosphorus Mining from Manure

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Phosphorus Removal Process
Buffer Systems in Animal Manure

Alkalinity
Ammoniacal Nitrogen

Urea Hydrolysis

\[ \text{CO(NH}_2\text{)}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{NH}_4^+ + \text{CO}_3^{2-} \]
Buffer Systems Make Difficult the Precipitation of Phosphorus in Liquid Manure:

Carbonate Buffer System prevents calcium phosphate formation

$$\text{Ca(OH)}_2 + \text{Ca(HCO}_3\text{)}_2 \not\Rightarrow 2\text{CaCO}_3 \not\leftarrow + 2\text{H}_2\text{O} \quad (2)$$

Ammonium – Ammonia Buffer System prevents calcium phosphate formation

$$\text{Ca(OH)}_2 + 2\text{NH}_4^+ \not\Rightarrow \text{NH}_3 \not\leftarrow + \text{Ca}^{++} + 2\text{H}_2\text{O} \quad (3)$$

High Amount of Chemical Required

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Phosphorus Removal Process

• The addition of Ca(OH)$_2$ (or Mg) after removal of natural buffers rapidly increases the pH, which promotes precipitation of phosphate with small amounts of chemical added.

Phosphorus Removal Concept:
Elimination of Buffer System with Biological Treatment

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Wastewater Treatment System Vanotti et al. U.S. Patent 6,893,567 B1
Phosphorus recovery from swine wastewater using Calcium Hydroxide

P removed from liquid (mg/L) with nitrification control

100%

Calcium hydroxide rates (Moles of Ca added/ mol P)

10 20 30 40 50 60

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On-Farm Treatment System

1. Swine Houses
2. Solid-liquid Separation Module
3. Nitrification Denitrification Module
4. Phosphorus Removal Module
5. Effluent
6. Calcium Phosphate
7. Reuse
8. Separated solids

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Manure treatment system developed to replace swine lagoons in North Carolina. NC Attorney General – Smithfield Foods/PSF Agreement

Goshen Ridge Farm, Duplin Co., NC
4,360-finishing pig production unit
Raw Manure Treated: 39 m³/day

Phosphorus Recovery Module

N treatment

Solid-liquid Separation
Soluble phosphorus separation and bagging of the calcium phosphate
Dewatering and bagging of calcium phosphate

Recovered P from sludge = 99.5%

Vanotti et al., Biores. Technol. 98:3184-3194
### Recovered Phosphates

#### Chemical Composition

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{P}_2\text{O}_5$</td>
<td>24.4% ± 4.5%</td>
</tr>
<tr>
<td>Calcium</td>
<td>27.3 %</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.9 %</td>
</tr>
<tr>
<td>Magnesium</td>
<td>1.8 %</td>
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</tbody>
</table>

99% plant available (standard citrate test)
Agronomic Effectiveness of Phosphates Recovered from Manure

Interaction with Industry
Production of fertilizer pellets

Green-house testing at Florence
Concentration of pathogen indicator in manure liquid (bacterial count/mL)

- Manure flush
- Separated liquid
- Biological N removal
- P effluent

THE HIGH PROCESS pH DISINFECTS THE EFFLUENT
SUMMARY

• Phosphorus is selectively precipitated using lime after carbonate and ammonia buffers are reduced with biological N removal.

• The precipitate is calcium phosphate (~ 24% P$_2$O$_5$) that can be reused as plant fertilizer.

• The high process pH also disinfects the effluent (> 4 logs)
Substantially eliminate:

1. ammonia emissions
2. odor emissions
3. pathogens
4. nutrient (N & P) surplus
5. heavy metal contamination

Lessons learned after testing 18 technologies at full-scale: a combination of two or more simple processes are needed to meet all environmental standards
Lower Cost, Second Generation Technology

NC Attorney General – Smithfield Foods Environmental Enhancement Program
SECOND GENERATION WITH SIMULTANEOUS SOLID-LIQUID SEPARATION OF SWINE MANURE AND PHOSPHORUS PRECIPITATE

Vanotti et al. (2010), U.S. Patent 7674379
Phosphorus removal module - continuous flow

Small P reactor (~ 1 m³ for 5400 pigs)

Application of lime to pH 9.5 and settling of calcium phosphate
Solid-liquid separation of manure and phosphorus with flocculation

High-capacity rotary press

Capture of P, organic N, Cu & Zn

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FLOCCULATION WITH POLYMERS INCREASES SOLIDS SEPARATION EFFICIENCIES

• PAM Applications: municipal, food processing, soil erosion, animal waste

• Absorb and bridge colloidal suspended particles into flocs

• Effective at low dosage

• Natural Polymers: Chitosan, Tanins

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Vanotti et al., Transactions of the ASAE, 1999, 2002, 2005
Model: Centralized Plant for Processing of Separated Manure Solids

Generation of Value Added Products through Composting

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Centralized Solids Processing Facility (Composting)

- Conserved the separated N and P
- Manure transformed into Class A compost
- Processed into plant growth media

<table>
<thead>
<tr>
<th>Nutrient Stabilization &amp; Recovery Solids Processing Facility</th>
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</thead>
<tbody>
<tr>
<td>Material Weight</td>
</tr>
<tr>
<td>Material Volume</td>
</tr>
<tr>
<td>Total Carbon</td>
</tr>
<tr>
<td>Total Nitrogen</td>
</tr>
<tr>
<td>Total Phosphorus</td>
</tr>
<tr>
<td>Total Zinc</td>
</tr>
<tr>
<td>Total Copper</td>
</tr>
</tbody>
</table>
Production of high-value plant growth media and organic fertilizers from composted manure
Another Phosphorus Recovery Technology

Quick Wash Process

Manure is washed with mild acids and then the phosphorus is recovered as solid
Poultry Litter Phosphorus Removal and Recovery
Quick Wash Process
USDA - ARS

1. P extraction
   Acidic solution

2. P removal
   Alkaline pH

3. P precipitation enhancement

Poultry Litter → Washed Litter → Recovered P → Liquid Effluent

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Manure Wash Pilot Experiment

1. Solid Manure + Water + Acid

2. Liquid with Low Suspended Solids + Soluble Phosphorus
   - Lime
   - Flocculant

3. Extracted Phosphorus Solids
   - Liquid to Recycle

Solid Manure + Water + Acid

Liquid with Low Suspended Solids + Soluble Phosphorus

Flocculant

Lime

Extracted Phosphorus Solids

Liquid to Recycle
Quick Wash
Products

Poultry litter after quick wash

P recovered from poultry litter

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Quick Wash for Pig Manure (Steps 2 & 3)

Process was optimized at pH 8

pH after step 1 = 4.3, then adjusted by addition of hydrated lime [2% Ca(OH)$_2$]

% TP Recovered = (P recovered /Initial P in fresh swine manure) x 100

Initial P in pig manure = 7.1 g/kg (30% solids)
Quick Wash for Pig Manure – Steps 2 & 3

TP recovery was greatly improved with anionic PAM application:

Flocculant = anionic polyacrylamide polymer applied at 7 mg/L
Quick Wash Process
Component of a Manure Management System

Land application
• Washed manure residue with higher N:P ratio

Nutrient transfer program
• Transport of a concentrated P material is more effective

Obj. 1: Advanced Management Systems
- 1a. Facilitate Adoption
- 1b. Solid-Liquid Separation
- 1c. N-removal
- 1e. P-extraction
- 1f. Microbial Assessment

Obj. 2: Thermochemical Conversion Technologies
- 2a. Feedstock Conditioning
- 2b. Pelletizing
- 2b. Combustible Gas & Biochar Production
- 2d. “Designer Biochar” Production
- CH₄, CO, H₂, etc.

Obj. 3: Impacted Riparian Buffers
- 3a. N₂O Emission Assessment
- 3b. Microbial Assessment
- 3c. Biochar Treatment

Obj. 4: Byproduct Uses
- 4a. Contaminant Adsorbant
- 4b. Improve Soil Fertility
- 4c. Improve Crop Production

Legend
- Physical Process
- Method/Assessment
- Information
Biochars produced from different feedstocks and at high/low temperatures

- Biochar can be made from various crop and manure feedstocks

- Biochar pyrolyzed at high/low temperatures will have different structural chemistries

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Manure Biochars as P fertilizer

Figure 1. Ryegrass growth response curve to chemical P fertilization and yield response to P added via livestock biochar (From Hunt and Cantrell, USDA-ARS, Florence.)
Nitrogen Recovery Technology with Gas Membranes
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
Microporous gas-permeable membrane: The ammonia gas (NH3) passes through

Liquid Manure

\[ \text{NH}_4^+ + \text{H}^+ \]

Strip solution (Aqueous acid)

\[ \text{NH}_3 + \text{H}^+ \]

\[ \text{H}^+ + \text{NH}_3 \]

\[ \text{NH}_4^+ \]

Hydrophobic Polymer (e-PTFE)

Gas-filled pore
For this research we used gas-permeable membranes made of expanded polytetrafluoroethylene (ePTFE) (Teflon). PTFE is stretched to form a strong, porous material.
Concept of Ammonia Capture from Wastewater using Gas Permeable Membrane

Air with Ammonia

Dirty Liquid with Ammonia

Membrane Pores

NH₃

H⁺ → NH₄⁺

Acidic Liquid

Membrane Pores

Ammonium Salt Fertilizer

Tubular or Flat Membrane Manifold Submerged in the Wastewater

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TUBULAR MEMBRANES
Removal of NH₃ from Liquid Manure Using Gas-Permeable Membranes

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Recovery and Concentration of Ammonia from Liquid Swine Manure using Gas Membranes (10 batches using same stripping solution)
Retrofit of manure storage units to harvest the ammonia

Anaerobic Livestock Wastewater Lagoon with Ammonia Recovery System

Nutrient Recovery System (N and P)

- **TREATED EFFLUENT**
- **AMMONIA & PHOSPHORUS SEPARATION REACTOR**
- **PHOSPHORUS PRECIPITATED SLUDGE**
- **RECOVERED AMMONIA**
- **DEWATERED MANURE SOLIDS, PHOSPHORUS & EXTRACTED NITROGEN**

**Components**:
- **CONFINED LIVESTOCK**
- **SWINE MANURE (SM)**
- **RAW WASTE**
- **HOMOGENIZATION TANK**
  - **MIXER**
- **SOLID SEPARATION UNIT**
- **LIME OR ALKALI DISPENSER**
- **MEMBRANE MANIFOLD**
- **TREATED EFFLUENT**

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Conclusions – N recovery from liquid manure

1. The use of gas-permeable membrane technology could be an effective approach to recover ammonia from livestock wastewater.

2. A concentrated liquid nitrogen is obtained that can be re-used in agriculture as a valued fertilizer.
http://www.ars.usda.gov/saa/cpswprc