

# JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

November 6, 2019

Volume 67 Number 44



Reclaiming Phosphate  
from Waste Solutions  
with Fe(III)-Polysaccharides

## MAXIMIZING THE BENEFIT, MINIMIZING THE HARM OF CAFO MANURE USED AS FERTILIZER

# Goals



Develop a process for converting the dilute manure from intense animal agriculture into a slow-release fertilizer



To reduce the loss of phosphorus and nitrogen from the use of manure on fields to grow crops



To make it much cheaper to transport manure to the locations where it will have more value and benefit



To make more money from manure while contributing to a reduction in HABs











# Manure: An Environmentally Sustainable Fertilizer



Manure contains nutrients that promote crop growth



Using it as fertilizer recycles nutrients in the animal's feed



Phosphorus supply is limited and declining

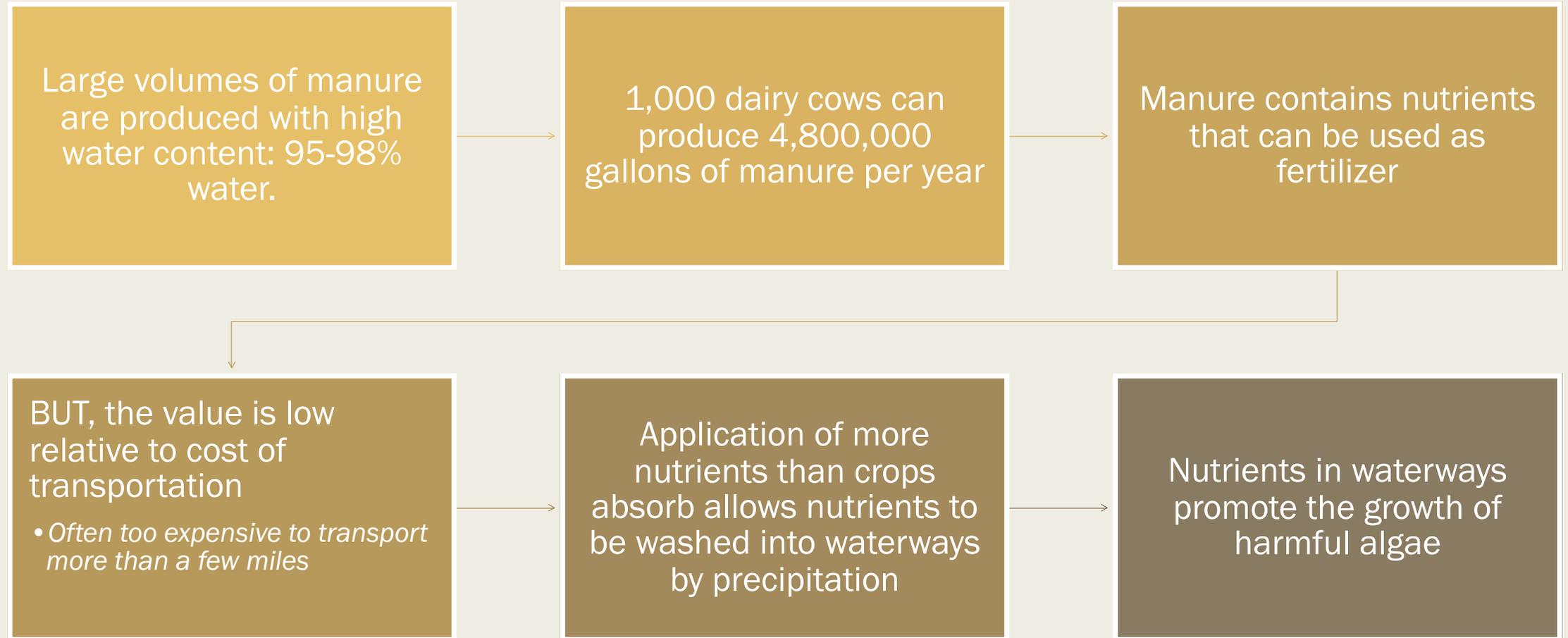


Need to find good ways to recycle phosphorus



HOWEVER ...

# The Problem





Separate the nutrients from the water

*Reduces weight by 20-40X – can transport 20-40X further at same cost*



Bind nutrients in a matrix that slowly releases them over the growing season

*Nutrients are available when crops need them most  
Less can be washed into waterways by precipitation*



This makes the product more valuable than the untreated manure



If product value exceeds cost of production, production can generate a profit



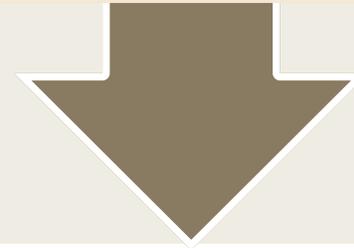
Profit can provide a financial incentive for reducing the risk of environmental harm from manure use

# The Solution

# Phase 1

Identify treatment processes in lab tests that work best with the types of dairy manure, soils, and crops that are common in the state of Ohio

*Key goal: treatment gross cost lower than \$0.03/gallon, net cost lower than \$0.01/gallon*



Test at the pilot-scale to confirm that the process optimized in the lab works in real fields

# Laboratory work to test & optimize the best methods for treating manure



Hundreds of lab tests conducted to identify best materials and process



Found two cationic polymers to be effective that work best with the addition of ferric chloride to enhance coagulation

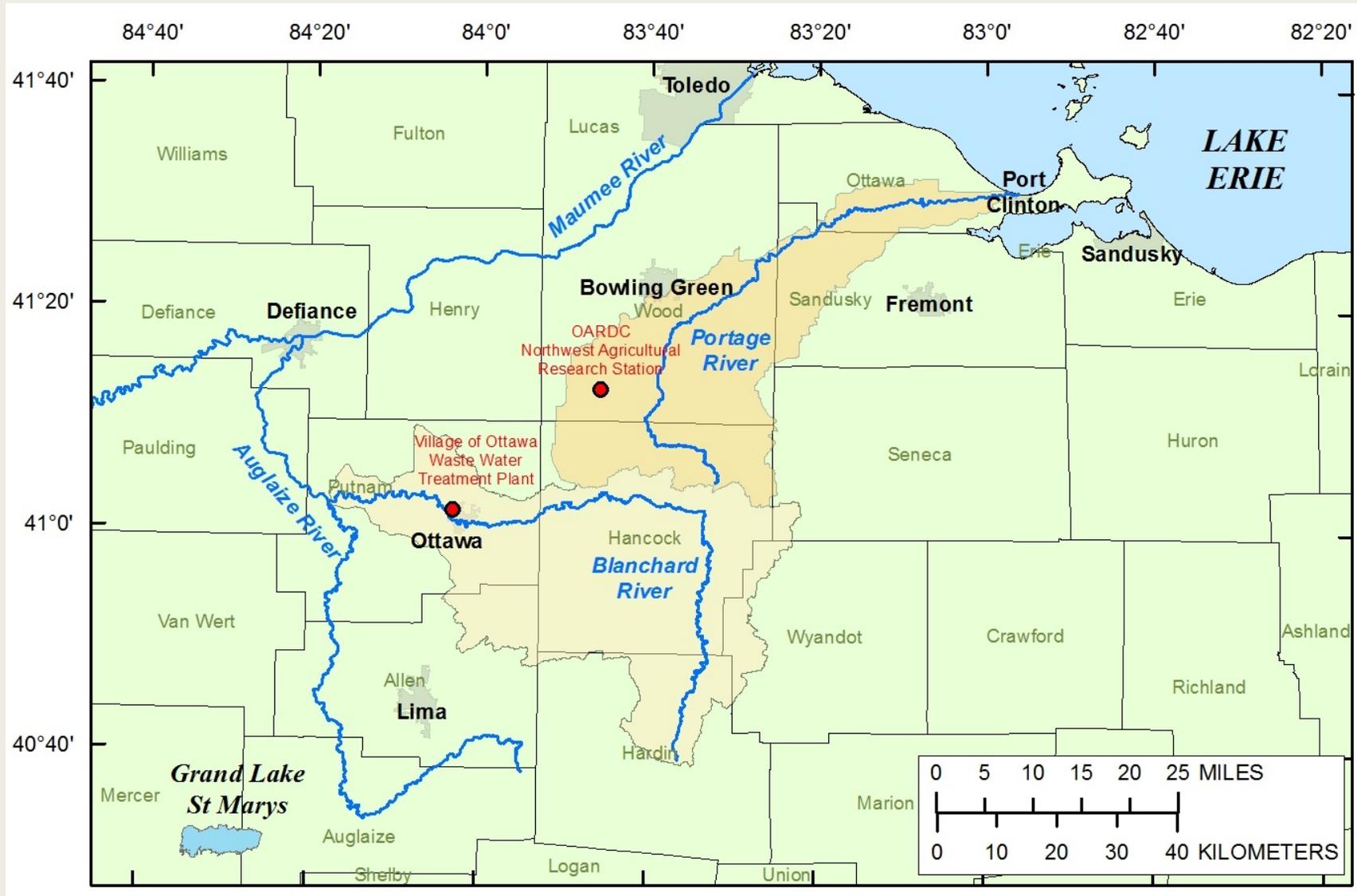


Soil columns used to determine nutrient release rates



Materials and treatment method selected that gave best results in the lab

# Pilot-Scale Study Location

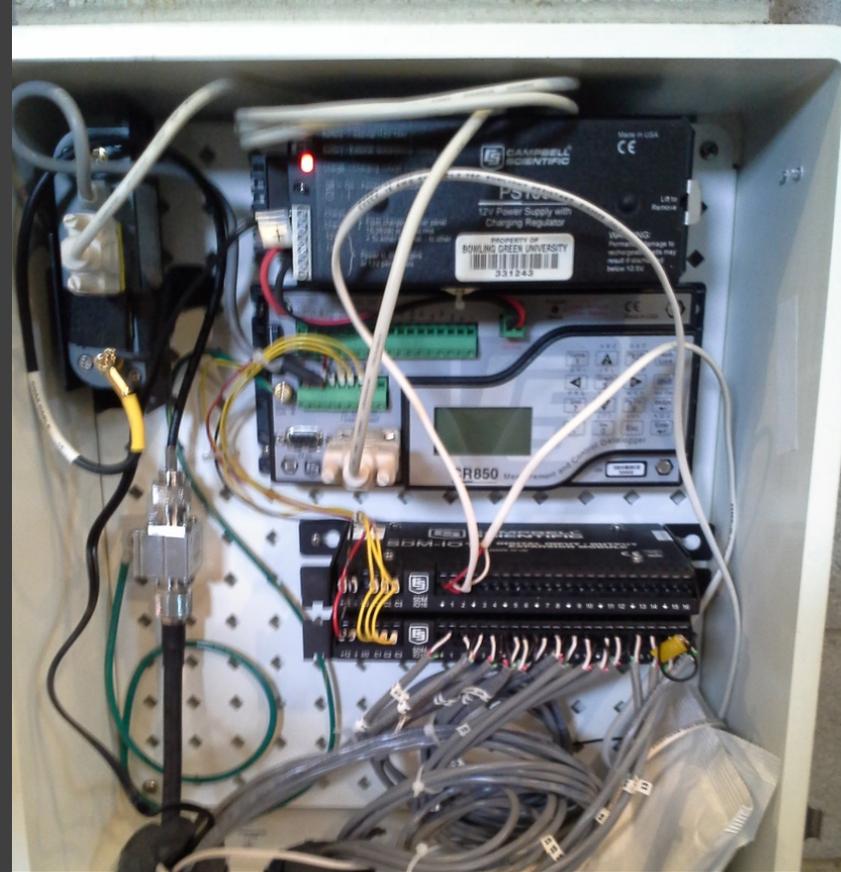




# Pilot-Scale Test Facility

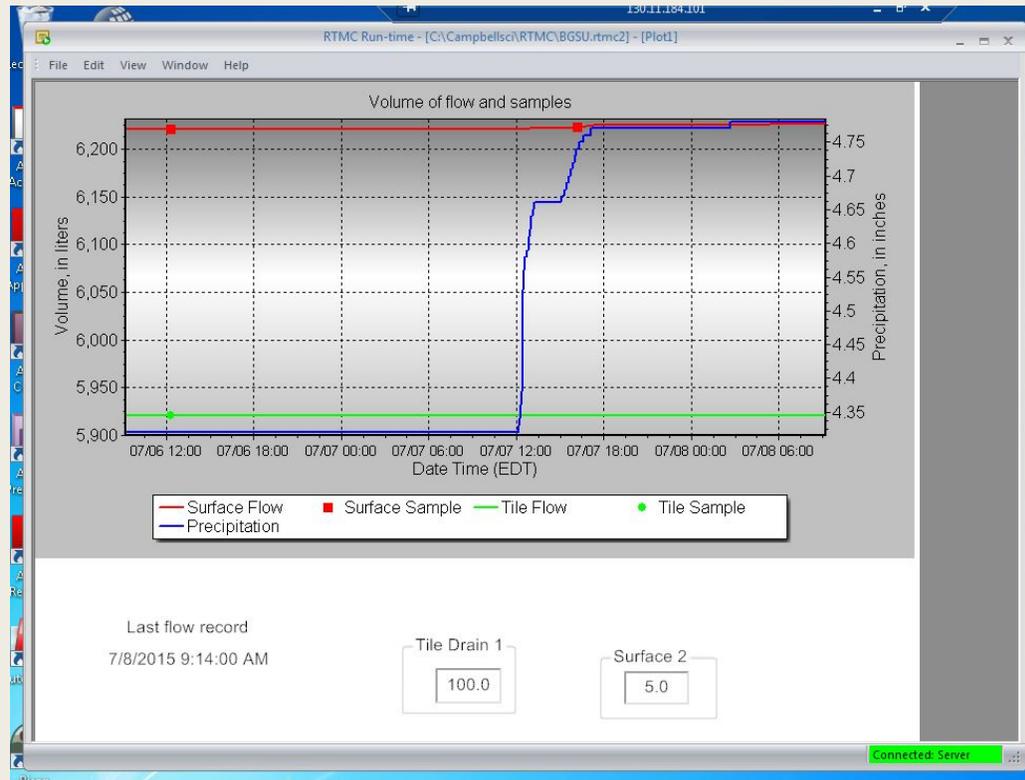
- Eight test plots where surface and subsurface (tile) runoff is transported to a central sheltered location
- 1. *Test equipment installed to measure variable flow*
- 2. *Collect and analyze runoff samples*
- 3. *Establish baseline conditions of the test plots*

**OSU OARDC Northwest Agricultural Research Station**



INSIDE: AUTOMATED SAMPLERS, TIPPING BUCKETS, MODEM COMMUNICATIONS

# Flow rate, volume, and sample reports



http://www.ohionowcast.info/BGSU\_Table.jpeg

File Edit View Favorites Tools Help

Page Safety Tools

Timestamp	Tile Count	Tile Volume	Surface Count	Surface Volume
7/15/2015 8:06:00 AM	11.00	100.00	3.00	12.80
7/15/2015 12:42:00 PM	12.00	96.80	3.00	12.80
7/17/2015 12:04:00 PM	1.00	15.24	0.00	0.00
7/17/2015 9:42:00 PM	2.00	50.40	0.00	2.40
7/18/2015 8:30:00 AM	3.00	50.40	0.00	2.40
7/18/2015 10:18:00 PM	3.00	45.60	1.00	20.00
7/18/2015 10:22:00 PM	3.00	46.40	2.00	16.00
7/18/2015 10:48:00 PM	3.00	72.00	3.00	16.00
7/18/2015 11:12:00 PM	4.00	101.60	3.00	2.40
7/19/2015 1:58:00 AM	5.00	100.00	3.00	7.20
7/19/2015 6:00:00 AM	6.00	100.00	3.00	7.20
7/19/2015 10:52:00 AM	7.00	100.00	3.00	7.20
7/19/2015 3:50:00 PM	8.00	100.80	3.00	41.60
7/19/2015 3:58:00 PM	8.00	9.60	4.00	42.40
7/19/2015 5:14:00 PM	9.00	102.40	4.00	7.20
7/19/2015 6:56:00 PM	10.00	100.00	4.00	8.00
7/19/2015 8:54:00 PM	11.00	100.00	4.00	8.80
7/19/2015 11:12:00 PM	12.00	100.80	4.00	9.60
7/20/2015 1:30:00 AM	13.00	100.80	4.00	9.60
7/20/2015 4:08:00 AM	14.00	100.00	4.00	9.60
7/20/2015 7:26:00 AM	15.00	100.00	4.00	9.60

# The Pilot-Scale Tests

---

Manure

Manure treated at Village of Ottawa  
WWTP

---

Compare

Compare the nutrient migration in soil  
of treated manure to that of raw  
manure

---

Monitor

Monitor surface and tile nutrient  
concentrations and flow

---

Determine  
and  
compare

Determine and compare nutrient  
runoff amounts and crop yields

---

# Project Team

## Bowling Green State University

- *Laboratory studies*
- *Collect and process field samples*
- *Analysis of samples for dissolved and total nutrients*
- *Polymer production, analysis, and testing*

## USGS Ohio-Kentucky-Indiana Water Science Center

- *Equipment installation, testing, programing, and maintenance*
- *Assist with quality control of chemical analysis*

## OSU OARDC Northwest Agricultural Research Station

- *Construct and maintain field plots and assist with access*
- *Services for land application of dairy manure and planting of row crops*

## Village of Ottawa, Ohio (Phase 2)

- *Large-scale manure treatment and transport*



PART OF  
THE  
PROJECT  
TEAM



Higher loads (amounts) were found for combined loads (surface and tile) in raw relative to treated plots for dissolved reactive phosphorus ( $p < 0.05$ )



Statistically significant differences were also found for flow-weighted mean concentrations



Suggests that dissolved reactive phosphorus was likely retained in the soil and hydrological transport was reduced for the plots amended with the treated manure as compared to raw manure



Crop yields were virtually the same on plots fertilized with raw and treated manure indicating the treated manure was as effective as raw as a fertilizer



This coagulant/polymer treatment shows potential in helping to reduce dissolved phosphorus in flow from agricultural fields with applied manure

# Findings

# Alginate & Pectin Polymers



The polymers found in the first phase technology do not capture ammonia



We have found that alginate & pectin polymers capture ammonia as well as phosphate

*Combined with iron or aluminum salts these materials are light sensitive*



These materials are considered to be safe for use in food



Alginate obtained from seaweed/kelp (macroalgae)



Pectin from fruit and fruit peel



But the purified, refined materials are too expensive (\$0.68/gallon)

# Next Steps

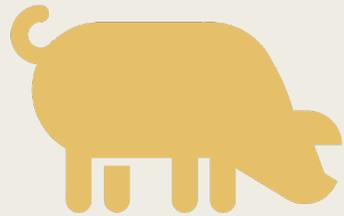
Test crude preparations and extracts of seaweed for effectiveness in manure treatment

- *macrocystis* (sea kelp), a monospecific genus of large brown algae;
- *ectocarpus*, such as *ectocarpus siliculosus*, a filamentous brown algae; and
- *Sargassum*, another type of brown algae but in the order *Fucales*, found in temperate and tropical oceans throughout the world that has become a huge problem in some areas of the Caribbean

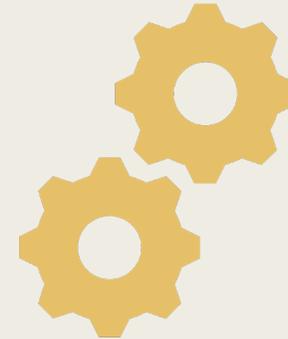
Also testing polysaccharides such as oxidized starch that are inexpensive but have properties that suggest they would be effective

- Carboxylate groups that bind metals such as iron, aluminum, and calcium

# Next Steps



Develop plans for a simple, automated farm-scale system that can use this process for treating manure



Minimize cost and optimize effectiveness to that this technology can be used throughout the region and beyond



## Benefits

- Lowered risk of adverse environmental impact of the use of a valuable agricultural material in an environmentally sustainable way
- More economical use of animal manure in locations where it can provide the most benefit
- Help to mitigate threats to our waters caused by HABs

# Contact Info

Dr. W. Robert (Bob) Midden  
Department of Chemistry  
304 University Hall  
Bowling Green State University  
(419) 372-0563  
midden@bgsu.edu

Dr. Alexis Ostrowski  
Department of Chemistry  
511 Physical Sciences Lab Building  
Bowling Green State University  
(419) 372-2809  
alexiso@bgsu.edu