Final Abstract

Final Report Approved on January 22, 2025

M.L. 2020 Project Abstract

For the Period Ending June 30, 2024

Project Title: Lignin-Coated Fertilizers for Phosphate Control

Project Manager: Eric Singsaas

Affiliation: U of MN - Duluth - NRRI

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Website: https://www.nrri.umn.edu/

Funding Source:

Fiscal Year:

Legal Citation: M.L. 2021, First Special Session, Chp. 6, Art. 5, Sec. 2, Subd. 08c

Appropriation Amount: $250,000

Amount Spent: $250,000

Amount Remaining: -

Sound bite of Project Outcomes and Results

Slow-release fertilizer coatings help prevent nutrient runoff from farms entering our watersheds, but the current coatings are not biodegradable, leaving significant microplastic contamination. Here, we have developed a proof-of-concept, biodegradable polymer coating that is compatible with current industrial spray-coating infrastructure and is made from lignin, a renewable wood product.

Overall Project Outcome and Results

The objective of this project was to develop a biodegradable formulation for a phosphate fertilizer coating. Currently, coated fertilizers are designed to mitigate the impact of fertilizer runoff by coating mineral fertilizer with a material that facilitates slow or controlled release. However, the prevailing generation of polymer coatings has been identified as a source of microplastics, which accumulate in the soil and subsequently enter waterways, contributing to microplastic pollution. To address this issue, we developed a biodegradable coating utilizing lignin. Lignin, an abundant and renewable byproduct, possesses several attributes that render it an ideal candidate for the primary component of a next-generation, slow-release fertilizer coating. Firstly, lignin is biodegradable, and its consumption by soil microbial communities is well-understood. Secondly, lignin exhibits hydrophobic properties, making it an ideal material for imparting moisture penetration resistance. Lastly, its inherent irregularity at the molecular level prevents material crystallization and results in a relatively low viscosity.

We developed a process for utilizing lignin derived from woody biomass, transforming it into a material that meets the demands of industrial spray-coating processes. Specifically, the lignin was devoid of flammable solvents and had a viscosity of ≤4,000 cP at or below 110°C. The isolated lignin was shear-mixed with a cross-linking reagent, which served as both a necessary component of the final polymer and a plasticizer to reduce viscosity prior to polymer curing. Ultimately, a prototype sample of a coated, polymerized superphosphate fertilizer was synthesized and subjected to accelerated weathering tests, demonstrating its ability to slow the release of phosphate. Future research will focus on optimizing release performance and cross-linking chemistries, as well as conducting biodegradation tests to confirm that the final coating products will disintegrate in soil environments.

Project Results Use and Dissemination

At this point, no public dissemination has been made relating to this project as IP potential for this technology is being considered. Detailed results from this project have been shared with the University of Minnesota's Technology Commercialization Office for review and consideration of patentability. All results classified as confidential for IP protection will be presented under nondisclosure agreements to interested parties, including, but not limited to, state agencies, federal agencies, non-governmental organizations, and companies interested in technology licensing for commercialization. We are in regular communication with representatives from the LCCMR to share updates on IP potential relating to this technology.

Environment and Natural Resources Trust Fund

M.L. 2020 Approved Final Report

General Information

Date: January 24, 2025

ID Number: 2020-077

Staff Lead: Mike Campana

Project Title: Lignin-Coated Fertilizers for Phosphate Control

Project Budget: $250,000

Project Manager Information

Name: Eric Singsaas

Organization: U of MN - Duluth - NRRI

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Project Reporting

Final Report Approved: January 22, 2025

Reporting Status: Project Completed

Date of Last Action: January 22, 2025

Project Completion: June 30, 2024

Legal Information

Legal Citation: M.L. 2021, First Special Session, Chp. 6, Art. 5, Sec. 2, Subd. 08c

Appropriation Language: $250,000 the second year is from the trust fund to the Board of Regents of the University of Minnesota for the Natural Resources Research Institute in Duluth to test a new, natural, slow-release fertilizer coating made from processed wood to decrease phosphorus runoff from farmland while also storing carbon in soils. This appropriation is subject to Minnesota Statutes, section 116P.10.

Appropriation End Date: June 30, 2024

Narrative

Project Summary: We will develop and test a novel, bio-based, fertilizer coating that slows nutrient release to reduce nutrient runoff from agricultural fields based on modified cellulose and lignin extracted from wood.

Describe the opportunity or problem your proposal seeks to address. Include any relevant background information.

This proposed project will provide a real-world test of a novel, bio-based, fertilizer coating that slows nutrient release to reduce nutrient runoff from agricultural fields. Anthropogenic phosphorus pollution is reaching dangerously high levels in freshwater basins around the world, with mineral phosphate fertilizers from cereal grain farming being among the largest contributing sources1. Phosphorus is a common component of both mineral and manure fertilizers because it is necessary to achieve high crop yields necessary to support conventional family farms in Minnesota. However, a large portion of phosphorus applied as fertilizer is not taken up by plants, and either builds up in the soil or washes into rivers, lakes, and coastal seas. Minnesota has implemented policies aimed at reducing agricultural runoff through wetlands preservation and increased buffer strips around fields. Another way to reduce fertilizer runoff is to coat fertilizer particles in a material that controls water diffusion so that the nutrients are released slowly over time, giving the crop roots a chance to absorb the fertilizer before percolation and runoff can remove the product. There has been work on developing slow-release fertilizers, but there remains a need to address issues of cost, performance, and effective implementation by farmers.

What is your proposed solution to the problem or opportunity discussed above? Introduce us to the work you are seeking funding to do. You will be asked to expand on this proposed solution in Activities & Milestones.

We are developing a technological solution to address this need. We will develop a slow-release fertilizer coating made from lignin, a byproduct of cellulosic ethanol production, that can be coated onto granulated fertilizers to control the rate of dissolution and thereby maintain a constant nutrient supply in fields without the need to over apply. This form of lignin has properties that allow it to be processed like a plastic, yet it is a 100% natural and biodegradable material made from wood. We are developing formulations with this material that can be coated onto granulated fertilizers to control the rate of dissolution and thereby maintain a constant nutrient supply in fields without the need to over apply. When the fertilizer is used up from a coated particle, the lignin coating becomes part of the slow-turnover carbon pool in the soil. Therefore, implementation of this technology throughout the agricultural sector has the potential both to decrease eutrophication and increase carbon sequestration.

What are the specific project outcomes as they relate to the public purpose of protection, conservation, preservation, and enhancement of the state's natural resources?

We will demonstrate the efficacy of a phosphate fertilizer coated with a novel, biodegradable coating for its ability to slow the release of nutrients in accelerated weathering tests relative to the current non-biodegradable coatings currently employed by the industry. NRRI is working with the University of Minnesota Technology Commercialization office to patent the technology and identify commercialization partners. Likely partners would include Minnesota-based agricultural fertilizer distributer Mosaic and Ohio-based Scotts for lawn and golf course markets. The results from this project are essential to attracting high-profile commercialization partners such as these that will add economic value to our state.

Project Location

What is the best scale for describing where your work will take place?

Statewide

What is the best scale to describe the area impacted by your work?

Statewide

When will the work impact occur?

In the Future

Activities and Milestones

Activity 1: Scale-up of lignin-material coated fertilizer and performance testing

Activity Budget: $58,675

Activity Description:
We will purchase 500 kg of granulated fertilizer and apply our best-performing lignin-based coating, developed in collaboration with colleagues from the Technical University of Cologne, Germany. This work will be done at NRRI's prototype laboratory using a pilot spheronizer. Plain Sight Innovations will supply organosolv lignin from their pilot plant for this activity. We will produce lignin for all greenhouse testing in Activity 2 in year 1. We will make formulation adjustments based on findings from greenhouse studies during scale-up for the field production to be conducted in Activity 3. Greenhouse and field trials will be supervised by Dr. Jane Johnson USDA-ARS scientist in Morris, MN and tasks will be preformed by student workers at UM-Morris. NRRI will support this work with chemical and statistical analyses and reporting.

Activity Milestones:

Description	Approximate Completion Date
Produce sample coated fertilizer for greenhouse testing	January 31, 2022
Measure phosphate dissolution rate compared to uncoated fertilizer	February 28, 2022
Scale-up production of fertilizer for greenhouse trials	May 31, 2022

Activity 2: Assess high lignin coating impact on soils in greenhouse

Activity Budget: $1

Activity Description:
A replicated (4x) and repeated (2x) greenhouse experiment will assess the ability of lignin-coated fertilizer to provide Phosphorus (P) to agronomic crop(s) as indicated by plant biomass accumulation at 30 days after planting. At the end of the study the amount of extractable P in the soil will be determined.

Activity Milestones:

Description	Approximate Completion Date
Description Greenhouse testing of lignin coated fertilizer	August 31, 2022
Chemical analysis of extractable phosphorus from greenhouse study	September 30, 2022
Plant growth and biomass accumulation measurements	September 30, 2022

Activity 3: Replicated field trials of lignin-coated fertilizer

Activity Budget: $1

Activity Description:
Replicated plot-scale field testing will assess agronomic crop (s), wheat or corn, response to incorporated lignin coated P fertilizer. The study will be repeated in at least 3-locations. We will plant the crop in May 2022 with fertilizers delivered from Activity 1. Crop will be managed through the summer of 2022 with harvest by October. Crop biomass and yield will serve as plant response indicators. Soil samples will be collected at two depth increments (0-15; 15-30 cm) at the end of the and assessed for extractable P. Samples will be collected during the growing season in the summer of 2022 and archived for analysis in the fall and early winter. Final data analysis will be complete in Q1 2023.

Activity Milestones:

Description	Approximate Completion Date
Description Plot-scale field testing to assess agronomic crop response	October 31, 2022
Crop biomass and yield analyzed	December 31, 2022
Soil sampling and processing	December 31, 2022
Extractable P measurements	January 31, 2023

Activity 4: Transformation of modified lignin feedstocks into spray coating-compatible mixtures

Activity Budget: $88,692

Activity Description:

The current process for coating fertilizers used by all manufacturers is spray coating. For a new coating formulation to be adopted by the industry, it must be compatible with their current infrastructure, as investments in entirely new coating processes are prohibitive. Fertilizer coatings are produced by spraying chemical precursors onto granules in a rotating drum which subsequently react with one another to form a polymer on the surface of the granule. The viscosity of the precursor chemicals (or precursor chemical mixture) must be below 4,000 centipoise at temperatures no greater than 110 °C to be compatible. Neat (pure) samples of modified lignin may not achieve desired viscosities and must be mixed with non-flammable plasticizers to achieve desired viscosities. Examples of spray coating-compatible plasticizers could be water or diethylene glycol, which will be introduced at minimum concentrations required to meet viscosity targets. Mixing the modified lignin samples with plasticizers will be performed by shear-mixing, and the resulting mixtures will be analyzed for their dynamic viscosities over various temperatures. Purchasing a shear mixer and variable-temperature viscometer is part of this task's budget.

Activity Milestones:

Description	Approximate Completion Date
Purchase, onboarding and training of new equipment	March 31, 2023
Variable temperature viscosity assessments of modified lignins (or mixtures)	June 30, 2023
Scale up viable candidates for subsequent experiments	August 31, 2023

Activity 5: Development of cross-linking (polymer formation) chemistries for coated fertilizer granules

Activity Budget: $60,192

Activity Description:

Modified lignins and their mixtures that met viscosity requirements in Activity 1 will be carried forward for the development of cross-linking chemistry methods. Employed cross-linking reagents will be polyfunctional and will act to link together deposited lignin fragments transforming the precursor coating into a continuous, macromolecular polymer coating. The cross-linking reagents may also serve as plasticizers and may be deposited on the granules concurrently with the lignin or modified lignin. All cross-linking reagents will be carefully chosen and will consider the types of bonds these reagents will form with the lignin or modified lignins. Various types of bonds are inaccessible to microbial degradation (e.g., polyurethane bonds) and will be avoided in the crosslinking chemistries performed here. Furthermore, the chemical reagents themselves must be considered non-toxic and/or biodegradable as to not introduce unwanted environmental contamination. Examples of cross-linking reagents which could be employed include polyols such as citric acid, diethylene glycol, and polyethylene glycol 600 or a dicarboxylic acid such as adipic acid. Polymerization chemistries will largely be developed as films on microscope slides and products with desirable properties (high thermal stability) will be carried forward for prototype production in Activity 3

Activity Milestones:

Description	Approximate Completion Date
Polymer development using polyols as cross-linking reagents	December 31, 2023
Polymer development using dicarboxylic acids as cross-linking reagents	December 31, 2023
Thermal stability (TGA-DTA) testing of produced polymer films	January 31, 2024

Activity 6: Production of coated fertilizer prototypes and accelerated weathering testing

Activity Budget: $42,439

Activity Description:

Polymer coatings produced on microscope films in Activity 2 will be translated to a process where the final polymer product is coated on the surface of a phosphate fertilizer granule. This will be done via drum-coating, a spheronizer or some other coating mechanism. Crosslinking chemistries and subsequent heating (if necessary) will also be performed so that a cured, stable polymer results on the surface of the granules. Coating thickness, controlled by the fertilizer to coating solution ratio used, will be varied and the impact the thickness has on the delay in fertilizer release will be assessed. All accelerated weathering tests will involve suspending the coated granules in water and leaving them under constant gentle agitation. Phosphate concentrations in the water will be assessed over time (up to two weeks) to quantify the release kinetics. These results will be juxtaposed with release rates from conventional fossil-fuel based coatings currently employed by the fertilizer industry.

Activity Milestones:

Description	Approximate Completion Date
Development of lab-scale coating process	March 31, 2024
Generation of protoype coated granules for accelerated weathering tests	April 30, 2024
Accelerated weathering tests	May 31, 2024

Dissemination

Describe your plans for dissemination, presentation, documentation, or sharing of data, results, samples, physical collections, and other products and how they will follow ENRTF Acknowledgement Requirements and Guidelines.

All potential intellectual property resulting from this program will be submitted to the University of Minnesota's Technology Commercialization office for review before public disclosure. All results classified as confidential for IP protection will be presented under nondisclosure agreements to interested parties including, but not limited to, state agencies, federal agencies, non-governmental organizations, and companies interested in technology licensing for commercialization. All protected and non-confidential results will be presented at a national or international agriculture or biomass conference. Publishable results will be written up for publication in a peer-reviewed scientific journal. All progress and results that are of interest to the public will be disseminated through social media, press releases, and other public means.

Long-Term Implementation and Funding

Describe how the results will be implemented and how any ongoing effort will be funded. If not already addressed as part of the project, how will findings, results, and products developed be implemented after project completion? If additional work is needed, how will this work be funded?

A key program deliverable is a product that will be sold into the agricultural fertilizer market. Our results will be implemented in attracting future funding form the fertilizer sector to finish bringing this product to market. We are actively communicating with several potential end-users of our material and include chemical supply companies and fertilizer companies. Another obvious next step for our prototype material would be to scale up production to perform a field trial in an agricultural setting. This could either be funded by the private sector or we could use our results here to go after federal grants.

Budget Summary

Category / Name	Subcategory or Type	Description	Purpose	Gen. Ineligible	% Benefits	# FTE	Classified Staff?	$ Amount	$ Amount Spent	$ Amount Remaining
Personnel										
Eric Singsaas		Project lead; will be responsible for project management, meetings, data analysis and reporting			25.1%	0.21		$34,690	-	-
Matthew Young		Bio-Process Engineer; Matt will lead the efforts in producing coated fertilizer prototypes			22.3%	0.15		$14,075	-	-
Oksana Kolomitsyna		Organics Chemist; Kolomitsyna will perform synthesis of new coatings prototype materials and assist with coatings application to phosphate fertilizers.			25.1%	0.72		$49,915	-	-
Brian Barry		Chemistry lead; supervise chemistry laboratory activities, including synthesis of coatings materials, analysis of prototype coating performance, and develop phosphate analysis work instructions.			25.1%	0.57		$53,377	-	-
Cally Hunt		Chemical engineer; will work on producing coated fertilizer prototypes			22.3%	0.15		$11,372	-	-
Alex Kacharov		Synthetic chemist; in charge of lignin modifications and cross-linking chemistry			25.1%	0.66		$44,574	-	-
							Sub Total	**$208,003**	**$208,003**	**-**
Contracts and Services										
							Sub Total	**-**	**-**	**-**
Equipment, Tools, and Supplies										
	Tools and Supplies	Analytical lab reagents	Reagents will be used to perform analyses NMR analysis on modified/polymerized lignin products					$1,000	$1,000	-

	Tools and Supplies	Solvents and reagents for coatings	Several chemical reagents and solvents will be required for lignin modifications and for the coating process					$1,003	$1,003	-
							Sub Total	**$2,003**	**$2,003**	**-**
Capital Expenditures										
		This expense is for the purchase of a shear mixer	Modified lignin products need to be intensely mixed with plasticizers to form flowable coating mixture	X				$9,979	$9,979	-
		Viscometer	This instrument will be used to perform variable temperature viscosity measurements on coating formulas to ensure compatibility with industrial processes	X				$30,015	$30,015	-
							Sub Total	**$39,994**	**$39,994**	**-**
Acquisitions and Stewardship										
							Sub Total	**-**	**-**	**-**
Travel In Minnesota										
							Sub Total	**-**	**-**	**-**
Travel Outside Minnesota										
							Sub Total	**-**	**-**	**-**
Printing and Publication										
							Sub Total	**-**	**-**	**-**
Other Expenses										
							Sub Total	**-**	**-**	**-**

							Grand Total	**$250,000**	**$250,000**	**-**

Classified Staff or Generally Ineligible Expenses

Category/Name	Subcategory or Type	Description	Justification Ineligible Expense or Classified Staff Request
Capital Expenditures		This expense is for the purchase of a shear mixer	The shear mixer will be a critical tool for our team to generate thoroughly homogenized mixtures of our modified lignin products with plasticizers to transform the material into a flowable mixture. This equipment will be necessary to complete the project. **Additional Explanation :** This shear mixer will continued to be used in developing recipes for spray coating compatible mixtures for the entirety of its useful life. These coatings will be explicitly targeting the application of slow-release fertilizers to reduce phosphorus runoff into Minnesota waterways.
Capital Expenditures		Viscometer	In order to determine whether or not our modified lignin products are compatible with industrial spray coating processes we must ensure that our mixtures do not exceed viscosity thresholds and this equipment will allow us to make those critical measurements. This equipment is necessary to complete this project. **Additional Explanation :** This viscometer will continued to be used in developing recipes for spray coating compatible mixtures for the entirety of its useful life. These coatings will be explicitly targeting the application of slow-release fertilizers to reduce phosphorus runoff into Minnesota waterways.

Non ENRTF Funds

Category	Specific Source	Use	Status	$ Amount	$ Amount Spent	$ Amount Remaining
State						
			State Sub Total	**-**	**-**	**-**
Non-State						
In-Kind	UMN unrecovered indirect costs are calculated at the UMN negotiated rate for research of 55% modified total direct costs.	Indirect costs are those costs incurred for common or joint objectives that cannot be readily identified with a specific sponsored program or institutional activity. Examples include utilities, building maintenance, clerical salaries, and general supplies. (https://research.umn.edu/units/oca/fa-costs/direct-indirect-costs)	Secured	$91,674	$91,674	-
			Non State Sub Total	**$91,674**	**$91,674**	**-**
			Funds Total	**$91,674**	**$91,674**	**-**

Attachments

Required Attachments

Visual Component

File: 78dad525-0cc.pdf

Alternate Text for Visual Component

Problem - Innovation - Impact visual overview.
Problem is eutrophication of MN lakes by fertilizer runoff
Innovation is a biodegradable coating for fertilizers
Impact is improved water quality through reduced fertilizer runoff...

Supplemental Attachments

Capital Project Questionnaire, Budget Supplements, Support Letter, Photos, Media, Other

Title	File
Signed background check form	4130fba7-768.pdf

Difference between Proposal and Work Plan

Describe changes from Proposal to Work Plan Stage

Milestone completion dates have been updated to reflect new project timeline from 2021-23. Lignin supplier is updated from Attis Innovations to Plain Sight Innovations.

Additional Acknowledgements and Conditions:

The following are acknowledgements and conditions beyond those already included in the above workplan:

Do you understand and acknowledge the ENRTF repayment requirements if the use of capital equipment changes?

Yes

Do you understand that travel expenses are only approved if they follow the "Commissioner's Plan" promulgated by the Commissioner of Management of Budget or, for University of Minnesota projects, the University of Minnesota plan?

N/A

Does your project have potential for royalties, copyrights, patents, sale of products and assets, or revenue generation?

Yes

Do you understand and acknowledge IP and revenue-return and sharing requirements in 116P.10?

Yes

Do you wish to request reinvestment of any revenues into your project instead of returning revenue to the ENRTF?

No

Does your project include original, hypothesis-driven research?

Yes

Does the organization have a fiscal agent for this project?

Yes, Sponsored Projects Administration

Work Plan Amendments

Amendment ID	Request Type	Changes made on the following pages	Explanation & justification for Amendment Request (word limit 75)	Date Submitted	Approved	Date of LCCMR Action
1	Amendment Request	• Narrative • Project Collaborators - Project Partner Info • Budget - Personnel • Budget - Professional / Technical Contracts • Activities and Milestones • Budget - Capital, Equipment, Tools, and Supplies • Budget - Travel and Conferences • Budget - Other	The original proposal included a sub-award to a USDA collaborator who, after the funding was approved, had to decline participation for various reasons. Because of this, we needed to make revisions to our work plan and budget. We concluded that further development and optimization of our coating material to better meet performance targets was a worthy pivot for this project and in fact may result in better overall outcomes.	February 13, 2023	Yes	February 14, 2023
2	Completion Date	Previous Completion Date: 06/30/2023 New Completion Date: 06/30/2024	Our collaborators at the USDA are no longer able to participate on this project which resulted in the need to revise our workplace and submit a rebudget. This has caused a significant delay in the project.	December 20, 2022	Yes	January 13, 2023
3	Completion Date	Previous Completion Date: 06/30/2024 New Completion Date: 12/31/2024	LCCMR workaround needed to approve April 2024 update.	July 18, 2024	Yes	July 18, 2024
4	Completion Date	Previous Completion Date: 12/31/2024 New Completion Date: 06/30/2024	LCCMR administrative workaround needed to approve April update.	July 18, 2024	Yes	July 18, 2024
5	Amendment Request	• Budget • Other • Budget - Travel and Conferences • Budget - Other • Attachments • Budget - Personnel • Budget - Capital, Equipment, Tools, and Supplies	We are requesting an amendment to rebudget the funding categories. All planning meetings were done over Zoom so no travel was needed. All biochar testing was completed in our labs, so no materials were shipped. Increased personnel time was needed to complete the analyses. The equipment cost less than expected. Less laboratory supplies were needed than initially anticipated.	January 9, 2025	Yes	January 10, 2025

Status Update Reporting

Final Status Update August 14, 2024

Date Submitted: January 9, 2025

Date Approved: January 10, 2025

Overall Update
The primary outcome we aimed to achieve for this project was to develop a lignin-based, biodegradable polymer that could be a drop-in replacement for the non-biodegradable, fossil-based polymers currently employed by the coated fertilizer sector. To be considered a suitable replacement, the material would need to be compatible with industrial spray-coating infrastructure, be devoid of flammable solvents, and have a viscosity of less than 4,000 cP below 110°C. Additionally, the material needed to have the ability to cure (polymerize) after being sprayed on the fertilizer granules. Any polymerization ahead of the coating process would render the material's viscosity too high for spray-coating. We have successfully developed several workable formulations that meet the aforementioned physical property and chemical reactivity requirements to be considered an acceptable replacement for the status quo, fossil-fuel-based coatings. A subset of the identified workable coating formulations were selected for use in producing coated phosphate fertilizer prototypes. These prototypes were subjected to accelerated weathering tests where the phosphate release over time was monitored relative to uncoated fertilizer samples. All of our prototypes revealed their ability to slow phosphate release and can be considered promising candidates for commercialization.

Activity 1
This activity was previously marked complete.
(This activity marked as complete as of this status update)

Activity 2
This activity was previously marked complete.
(This activity marked as complete as of this status update)

Activity 3
This activity was previously marked complete.
(This activity marked as complete as of this status update)

Activity 4
From our unrefined, mixed hardwood organosolv lignin feedstock (produced externally), we extracted in bulk with ethanol, followed by filtering and then removing the solvent from the supernatant to yield our low molecular weight lignin (LMWL) with ~80% recovery. This LMWL was the starting material for various chemical modifications, including succinylation, esterification, and base-induced degradation. These modified lignin materials were subsequently mixed with a plasticizer (polyethylene glycol 400) and heated to ~80 °C to melt the mixture before undergoing shear mixing. The homogenized mixtures then had their viscosities measured over a range of temperatures (50-150 °C) to determine if the samples' viscosity came in below our targeted value (<4,000 cP). We found ten combinations of various modified lignins mixed with a plasticizer suitable for carrying forward to activity five as they achieved a low enough viscosity to be used in industrial spray-coating processes. Attachments found in tab 7 of the grant management portal detail the chemical modifications performed on the lignin and the results of the variable-temperature viscosity experiments of the lignin (or modified lignin) mixed with various plasticizers.
(This activity marked as complete as of this status update)

Activity 5
For this portion of the project, we developed chemical pathways to crosslink (polymerize) our modified lignin. This included testing out various acid catalysts, reaction temperatures, and reaction durations. For initial crosslinking

chemistry assessments, samples of lignin (or modified lignin, ~2g) and the crosslinking agent were shear mixed before loading the mixture into a 100 mL Teflon beaker. Next, a small amount (0.1- 0.3 mL) of acid catalyst (e.g., concentrated H_2SO_4) was dropped into the Teflon beaker and stirred with a glass stir rod before heating overnight in an oven at 120 °C. When successful, the resulting "pucks" of product from these experiments revealed a solid, often rubbery material, clearly indicating the success of the polymerization chemistry. See an attachment in tab 7 of the grant management portal for images of polymerized products generated from this portion of the project. Our best results, as expected, came from reacting our succinylated lignin materials with various diols (e.g., polyethylene glycol). We chose three material mixtures, all including succinylated lignin mixed with polyethylene glycols of various molecular weights (400-2000 Da), to move forward for accelerated weathering tests as part of activity 6.
(This activity marked as complete as of this status update)

Activity 6
For this activity we translated the chemistries developed in Activity 5 into a coating process to produce coated phosphate fertilizer prototypes to be assessed in accelerated weathering tests. To achieve this, ~20 g of phosphate fertilizer granules were placed in a small, rotating drum coater. The unpolymerized lignin mixture (unpolymerized) was then dripped onto the tumbling granules until all particles appeared to be evenly coated. Next, the acid catalyst was dripped onto the coated fertilizer granules, which was allowed to tumble for 30 minutes at ~150 °C. Without this initial polymerization, the added lignin mixture would remain sticky and viscous, causing the granules to clump upon cooling. It would not allow for complete coating coverage on the individual granules. After 30 minutes, the coated samples were spread out into a single layer on a sheet pan and placed in a 120 °C oven overnight to complete the curing of the polymer. A series of coated fertilizer prototypes made from succinylated lignin and polyethylene glycol were selected for accelerated weathering tests, revealing that our coatings effectively slowed phosphate release. These results have been uploaded into tab 7 of the grant management portal.
(This activity marked as complete as of this status update)

Dissemination
No dissemination during this period. We are discussing patentability with the Technology Commercialization office but await acceptance from a commercialization partner before pursuing a patent. We will provide a final technical report once a patent decision has been made or a patent has been filed. All submitted papers and public-facing reports will be uploaded as attachments.

Additional Status Update Reporting

Additional Status Update August 14, 2024

Date Submitted: May 29, 2024

Date Approved: July 18, 2024

Overall Update
Per LCCMR staff guidance, due to system logic, this is placeholder text for update to be submitted by August 14, 2024

Activity 1
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Activity 2
This activity was previously marked complete.
(This activity marked as complete as of this status update)

Activity 3
This activity was previously marked complete.
(This activity marked as complete as of this status update)

Activity 4
Per LCCMR staff guidance, due to system logic, this is placeholder text for update to be submitted by August 14, 2024

Activity 5
Per LCCMR staff guidance, due to system logic, this is placeholder text for update to be submitted by August 14, 2024

Activity 6
Per LCCMR staff guidance, due to system logic, this is placeholder text for update to be submitted by August 14, 2024

Dissemination
Per LCCMR staff guidance, due to system logic, this is placeholder text for update to be submitted by August 14, 2024

Status Update Reporting

Status Update April 1, 2024

Date Submitted: May 29, 2024

Date Approved: July 18, 2024

Overall Update
The primary outcome we aimed to achieve for this project was to develop a lignin-based, biodegradable polymer that could be a drop-in replacement for the non-biodegradable, fossil-based polymers currently employed by the coated fertilizer sector. To be considered a suitable replacement, the material would need to be compatible with industrial spray-coating infrastructure and must be devoid of flammable solvents and have a viscosity less than 4,000 cP below 110 C. Additionally the material needed to have the ability to cure (polymerize) after being sprayed on the fertilizer granules. Any polymerization ahead of the coating process would render the material's viscosity too high. To date we have successfully developed several workable formulations that meets all of the requirements to be considered an acceptable replacement. The only task left for us to complete is activity 6, where we will test our prototype lignin-coated fertilizers for their phosphate release performance in accelerated weathering tests.

Activity 1
This activity was previously marked complete.
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Activity 2
This activity was previously marked complete.
(This activity marked as complete as of this status update)

Activity 3
This activity was previously marked complete.
(This activity marked as complete as of this status update)

Activity 4
From our unrefined, mixed hardwood organosolv lignin feedstock (produced externally), we extracted in bulk with ethanol, followed by filtering and then removing the solvent from the supernatant to yield our low molecular weight lignin (LMWL) with ~80% recovery. This LMWL was used as the starting material for various chemical modifications including succinylation, esterification and base-induced degradation. These modified lignin materials were subsequently mixed with a plasticizer (e.g., polyethylene glycol 400) and heated to ~80 C to melt the mixture before undergoing shear mixing. The homogenized mixtures then had their viscosities measured over a range of temperatures (50-150 C) to determine if the samples viscosity came in below our targeted value (<4,000 cP). We found 10 combinations of various modified lignins mixed with a plasticizer that were suitable for carrying forward to activity 5 as they achieved a low enough viscosity to be used in industrial spray-coating processes.
(This activity marked as complete as of this status update)

Activity 5
For this portion of the project we developed chemical pathways to crosslink (polymerization) our modified lignin. Polymerizing the lignin is necessary to produce a material capable of slowing down the intrusion of water through the fertilizer coatings when in a soil environment. This included testing out various acid catalysts, reaction temperatures and reaction durations. It should be noted that the added plasticizers served two roles, one to lower the viscosity of the material, and two, to act as the cross linking reagent. Our best results, as expected, came from reacting our succinylated lignin materials with various diols (e.g., polyethylene glycol). We chose 3 material mixtures, all including succinylated lignin mixed with polyethylene glycols of various molecular weights (400-2000 Da) to move forward for accelerated

weathering tests as part of activity 6.
(This activity marked as complete as of this status update)

Activity 6
This activity is currently underway and can be considered 90% complete. For this activity we first onboarded a colorimetric method for quantifying phosphate concentrations in aqueous solutions. This test will be used to monitor the release of phosphate during our accelerated weathering tests. The accelerated weathering tests are quite simple and involve placing 2 grams of coated (or uncoated) fertilizer in a Nalgene container with 50 mL of DI water. These containers were then placed on an orbital shaker for gentle agitation. Aliquots of the water from these containers were withdrawn at predetermined time intervals to be tested for their phosphate concentration. A plot of the phosphate concentration vs time will be generated and overlaid with phosphate concentration data for uncoated samples to reveal the coatings performance. The accelerated weathering tests will be completed by mid June.

Dissemination
We have no dissemination activities to report at this time.

Status Update Reporting

Status Update October 1, 2023

Date Submitted: October 8, 2023

Date Approved: January 3, 2024

Overall Update
The primary outcome of this project is to "…demonstrate the efficacy of a phosphate fertilizer coated with a novel, biodegradable coating for its ability to slow the release of nutrients in accelerated weathering tests relative to the current non-biodegradable coatings…". Since the last update, we have bought two pieces of equipment, a shear mixer and a rotational viscometer, and have developed methods for testing our materials in variable temperature viscosity experiments. We have completed ~80% of the viscosity measurements (Activity 4) and produced several materials that meet the requirements to be carried through to Activity 5. Activity 5 has been started and is approximately 10% complete. Overall, the progress made to date on this project leaves us well-positioned to complete all activities and objectives for this project by the end of June 2024.

Activity 1
This activity was previously marked complete.
(This activity marked as complete as of this status update)

Activity 2
This activity was previously marked complete.
(This activity marked as complete as of this status update)

Activity 3
This activity was previously marked complete.
(This activity marked as complete as of this status update)

Activity 4
Since the last project update, we have installed and have been trained on using two new pieces of equipment: a rotational viscometer and a shear mixer. Methods and protocols for carrying out lignin(and lignin mixtures) viscosity measurements were developed, and the corresponding work instruction documents were completed. The targets for this task were to produce lignin-based materials and material mixtures that achieved viscosities below 4,000 centipoise at temperatures not to exceed 110 °C. These mixtures were also required to be devoid of any volatile or flammable materials (e.g., organic solvents). To this end, we tested 20 lignin and lignin mixtures under a range of temperatures (room temperature up to 150 °C), and several samples met these viscosity and temperature requirements. This work is currently ~80% complete, as we still want to test a few more mixtures.

Activity 5
Beginning this task required that lignin or lignin mixtures were identified for meeting viscosity requirements (Task 4) before cross-linking attempts started. As such, the last project update indicated that this task had not started. Since we have most of the work done for Activity 4, we were able to start exploring cross-linking chemistries. We have started to identify successful cross-linking catalysts by inspecting the physical state of the cross-linking products relative to their state before cross-linking. In a typical experiment, the material is in a liquid or waxy state before cross-linking and is solid when cross-linked. This simple assessment allows us to identify reagent ratios and acid catalyst identities that result in successful cross-linking. The work on this activity is ~10% complete.

Activity 6
Work on this activity has not begun as it requires Tasks 4 and 5 to be completed first to inform decisions for the coating strategies to produce prototype lignin-coated fertilizer samples.

Dissemination
No dissemination this period.

Status Update Reporting

Status Update April 1, 2023

Date Submitted: May 3, 2023

Date Approved: May 4, 2023

Overall Update
Most of the effort for this reporting period was spent on reworking the work plan and the budget for the project as a significant pivot was required upon losing USDA-ARS as a partner. This included getting a new budget approved by the University's sponsored programs office and the LCCMR. The new work plan includes producing lignin or modified lignin mixtures to lower the mixture viscosity. To do this, we needed to purchase a shear mixer and a viscometer, both of which have been ordered and will arrive soon. Once onboarded, these new pieces of equipment will enable us to proceed more quickly with our new work plan. It should also be noted that a 1- year extension was requested and approved for this project.

Activity 1
No further work will be carried out under Activity 1. Based on the results from the earlier work completed and the loss of the partnership with USDA-ARS, we have pivoted to further development and optimization of our coating material under Activity 4, 5, and 6, as approved in our recent amendment.
(This activity marked as complete as of this status update)

Activity 2
As reported previously, this work was to be performed with USDA-ARS in Morris, MN. The USDA-ARS leadership concluded that the terms and conditions in the current LCCMR contract are unacceptable. Given this loss of partnership and the learnings in Activity 1, we can no longer complete this work as described, and instead will pursue efforts under Activity 4, 5, and 6, as approved in our recent amendment.
(This activity marked as complete as of this status update)

Activity 3
As reported previously, this work was to be performed with USDA-ARS in Morris, MN. After months of negotiations, USDA concluded that the terms and conditions in the current LCCMR contract are unacceptable. Given this loss of partnership and the learnings in Activity 1 we can no longer complete this work as described, and instead will pursue efforts under Activity 4, 5, and 6, as approved in our recent amendment.
(This activity marked as complete as of this status update)

Activity 4
The new budget was just only recently approved (March 2023), so spending or personnel time could not be used until a short time ago. This budget approval was also necessary to be completed before the purchase of two vital pieces of equipment could be completed. Since the budget was approved, we have completed the purchase order through the University's purchasing protocol and expect both pieces to arrive at NRRI in May. Once this equipment is installed, we will test our materials and optimize formulations for decreased viscosities.

Activity 5
Work on this activity has not begun as it requires Task 4 to be completed first to inform decisions for the synthetic strategies to be used on this task.

Activity 6
Work on this activity has not begun as it requires Tasks 4 and 5 to be completed first to inform decisions for the coating strategies to produce prototype lignin-coated fertilizer samples.

Dissemination

No dissemination this period.

Status Update Reporting

Status Update October 1, 2022

Date Submitted: February 13, 2023

Date Approved: February 14, 2023

Overall Update

We spent most of the last project period dealing with setbacks caused by loss of USDA-ARS as a technical partner. The other partner, Plain Sight Innovations, has been acquired by a larger firm, Comstock Inc., who are currently in negotiations with the U of Minnesota regarding further research partnerships. We have met with three companies in the fertilizer and related industries who could be partners to carry this work forward. Our new objective will be to create a formulation that is acceptable to our commercial partnerships to carry forward for field trials funded by industry.

Activity 1

We completed the coating trials using the originally proposed formulation. While the coatings were possible the performance was not sufficiently improved relative to uncoated fertilizers to warrant further development of the originally proposed coating. Through consultation with the fertilizer industry we have developed new formulations that are more compatible with industrial coating processes. We will submit an amendment describing our approach to developing new formulations based on this learning. The new formulations will still be made from lignin extracted from processed wood. This will ease the adoption of biodegradable coatings without requiring costly investment in new processing equipment.

Activity 2

This work was to be performed with USDA-ARS in Morris, MN. The USDA-ARS leadership concluded that the terms and conditions in the current LCCMR contract are unacceptable. Given this loss of partnership and the learnings in activity 1 we can no longer complete this work as described. We will submit a project amendment for this activity that furthers the technical goals of the new coating formulation.

Activity 3

This work was to be performed with USDA-ARS in Morris, MN. After months of negotiations USDA concluded that the terms and conditions in the current LCCMR contract are unacceptable. We are currently seeking partners for this work. Given this loss of partnership and the learnings in activity 1 we can no longer complete this work as described. We will submit an amendment for this activity that furthers the technical goals of the new coating formulation.

Dissemination

No dissemination this period.

Status Update Reporting

Status Update April 1, 2022

Date Submitted: April 20, 2022

Date Approved: May 5, 2022

Overall Update

Most effort this period has gone towards the preliminary work of contracting, clarifying roles and relationships, and project kick-off. The University of Minnesota and USDA-ARS are still negotiating a contract with USDA-ARS over the intellectual property provisions. We are moving forward with the preliminary project phases choosing to remain optimistic that these issues will be resolved in time to support the field work with USDA-ARS. The team members from NRRI and USDA met by videoconference on December 3, 2021 to kick off the project and review the project plan. We evaluated project goals and timelines and will make adjustments to make sure that the research gets back on track to meet our objectives.

One other change to note is that the lignin supplier, formerly Plain Sight Innovations, was purchased by Comstock Mining, Inc. out of Reno, NV. Comstock's management remains supportive of this project. They have made investments into their pilot plant to increase production of lignin and have accelerated plans to develop a commercial-scale biorefinery in Minnesota.

Activity 1

We purchased 25 kg of uncoated orthophosphate fertilizer granules for preliminary coating experiments. This was purchased using non-ENTRF funds because we wished to evaluate the material before the funds were awarded. We began work on pre-processing the lignin from Plain Sight Innovations (now Comstock) to pre-process it for a simplified water-based spray coating method. Pre-processed lignin was shipped to collaborators at the Technical University of Cologne (unpaid collaborators) to test a simplified method for forming water-based suspensions.

Activity 2

Work on this activity has not yet begun.

Activity 3

Work on this activity has not yet begun.

Dissemination

There was no dissemination during this period.