Environment and Natural Resources Trust Fund (ENRTF) M.L. 2015 Work Plan

Date of Report: 10/15/2014

Date of Next Status Update Report: Dec.31, 2015

Date of Work Plan Approval:

Project Completion Date: June 30, 2017

Does this submission include an amendment request? __

PROJECT TITLE: Preventing Phosphorous, Nitrogen and Pesticides from Entering Water Resources Through Draintiles

Project Manager: Kenneth J. Valentas

Organization: University of Minnesota

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Location: Statewide

Total ENRTF Project Budget: 100%	**ENRTF Appropriation:**	**$505,000**
	Amount Spent:	**$0**
	Balance:	**$505,000**

Legal Citation: M.L. 2015, Chp. 76, Sec. 2, Subd. 04d

Appropriation Language:

$505,000 the first year is from the trust fund to the Board of Regents of the University of Minnesota to develop a new nanocomposite material made from biomass that is designed to adsorb phosphorus, nitrogen and pesticides from stormwater and drain tile runoff discharge for recycling back to agricultural lands. This appropriation is subject to the requirements in

Minnesota Statutes, section 116P.10.

I. PROJECT TITLE: Preventing Phosphorous and Pesticides from Entering Water Resources Through Draintiles

II. PROJECT STATEMENT:

We have a new way of protecting Minnesota's waters and fisheries from the excess fertilizer (phosphorous and nitrates) and pesticide discharges of cities and farms. It involves novel **engineered hydrochars (nanocomposite material)** made from waste biomass that preliminary experiments have shown to be **effective in adsorbing phosphorous, pesticides and possibly nitrogen from water, such as in draintiles,** and preventing them from entering water resources. Once phosphorous, nitrogen and pesticides enter our water resources it is difficult and expensive to remove them. The simple solution is to prevent them from entering the waterways.

Hydrochar is made by a process called Hydrothermal Carbonization (HTC) that consists of heating aqueous biomass in a confined vessel to a temperature of about 400 ^{0}F and pressure of 260 psia for about 30 minutes. In this time the biomass solids are dehydrated by elimination of oxygen and hydrogen in the form of water. Almost no carbon dioxide is generated and the process is energy efficient because very little water is vaporized. This process converts the biomass slurry to an insoluble, carbon–rich hydrochar and a liquid filtrate containing nitrogen, phosphorous, potassium and reaction products of sugars and protein originally present in the biomass. Simple filtration is utilized to easily separate the hydrochar and filtrate for subsequent applications.

The engineered hydrochars that will be utilized in this project are of two types. First, by the addition of certain metal salts, such as magnesium chloride, the hydrochar's capacity for the adsorption of phosphorous can be enhanced significantly. Another type of hydrochar is designed, through the conditions specified in its manufacture, to essentially be a "sponge" for absorbing organic chemicals and pesticides from aqueous solutions such as leachate and draintile runoff. These hydrchars can be made from various biomass sources including glucose, sweet dairy whey, condensed distillers solids (a by-product of the ethanol industry), swine manure and cattle manure.

Engineered hydrochars) could be utilized in two ways in the field. First they could be used in tandem in a two-component filter situated at the discharge of a draintile (a point source). The first filter element would be the pesticide "sponge" to absorb pesticide that is dissolved in the drainltile runoff. The effluent from the first filter would subsequently flow through the second filter, a phosphorous adsorbing hydrochar. The first filter effectively traps pesticides so they can be removed from the draintile runoff before it reaches any water resource. The hydrochar with entrapped and bound pesticides can be eliminated in an environmentally neutral manner such as incineration for power generation or microbial degradation to harmless components. The second engineered hydro char with "bound" phosphorous and possibly nitrogen **can be recycled to the agricultural lands as a slow release soil amendment and fertilizer. A second approach is directed at phosphate and pesticides that leach with rains and seep into the surface and ground water and are not captured in draintiles. In this case the pesticide absorbing hydrochar that can also be engineered to bind phosphorous is incorporated into the soil itself to intercept pesticides and phosphorous before they reach any water sources. This second approach is contingent on soil bacteria breaking down the pesticides to harmless components at a rate consistent with the rate of breakdown of the hydrochar itself. In either situation** the net effect is keeping these unwanted nutrients and pesticides out of the waters and at the same time reducing the overall fertilizer use through recycling by minimizing the loss of nutrients from leaching.

Preliminary experiments in our laboratory have shown that a hydrochar treated with magnesium chloride and heated (600^0 C) in an inert Argon atmosphere to produce a magnesium oxide-hydrochar effectively removed 69% of the phosphorous in a challenge solution. Subsequent experiments have been directed at making a metal oxide –hydrochar composite without any post thermal treatment. This would be the preferred approach.

Absorption tests with several pesticides utilizing a simple HTC hydrochar made from ethanol thin stillage strongly support the proposition that organic solutes such as these pesticides can be effectively removed from water even at low concentrations.

Denitrification bioreactors that utilize woodchips can remove some of the nitrates from drainage water but this is converted to nitrogen that has no value for recycling to the land. Phosphorous is often the limiting nutrient in aquatic ecosystems and the main culprit in eutrophication. To date, minimal progress has been made in reducing dissolved phosphorous losses from cities and agricultural lands. Excess pesticides in either the soil or in leachate that ends up in our waters can seriously impact fisheries, human consumption in drinking water, or the population of agriculturally important insects such as pollinating bees.

Overall Goal: We propose to take a significant step in minimizing phosphorous, pesticides and possibly nitrate pollution through a novel mitigation process based on engineered hydrochars, recently developed at the University of Minnesota, that removes these chemicals from draintile water and recycles the phosphorous and nitrogen back to agricultural lands in the form of a slow release hydrochar fertilizer that is also beneficial to the soil microbial community. Specifically this will include;

(1) An engineered hydrochar designed to adsorb phosphorous and nitrates from agricultural drainage water and have utility as a soil amendment that can be recycled to the agricultural land as a fertilizer (possibly slow release) to reduce loss of nutrients through leaching.

(2) An engineered hydrochar specifically designed to absorb pesticides from agricultural drainage water, that can be subsequently incinerated or alternatively bioremediated to render the pesticides harmless.

(3) A hydochar designed to simultaneously adsorb phosphorous and absorb pesticides from agricultural drainage water.

(4) An effective and affordable engineered hydrochar filter for adsorbing phosphorous, pesticides and possibly nitrates in water from drain-tiled land.

Work Plan: We propose to:

- Evaluate engineered hydrochars, made from several biomass sources, for effectiveness in adsorbing phosphorous and nitrates, and absorbing pesticides from soil leachates under various production conditions.
- Determine the sorption/desorption efficiency of various engineered hydrochars and delineate critical design parameters for the design of laboratory scale filters.

- Design and construct a laboratory scale engineered hydrochar filter for use in removal of phosphorous, pesticides and nitrates from drain-tile effluents.
- Measure emissions from incineration of pesticide containing hydrochar to confirm environmental and human safety.
- Determine effects of hydrochar fertilizers on soil microbial community for principal Minnesota soil types.
- Investigate bioremediation potential of soil bacteria for pesticide containing hydrochars.

- Develop a quantitative long -term phosphorous management protocol based on experimentally determined sorption/decomposition properties of engineered hydrochars.

III. OVERALL PROJECT STATUS UPDATES:

Project Status as of *[Dec. 31, 2015]***:**

Project Status as of *[July 30, 2016]***:**

Project Status as of *[Dec. 31, 2016]***:**

Overall Project Outcomes and Results: July 30, 2017

IV. PROJECT ACTIVITIES AND OUTCOMES:

Activity 1: **Make and evaluate engineered hydrochars for phosphorous, nitrogen and pesticide sorption.**
Description: Determine efficacy of engineered hydrochars made from various biomass sources such as fermentation residues (condensed distillers solubles), dairy whey, manures, glucose and various activating metals such as magnesium, calcium, lanthanum and zirconium.
There are three (3) approaches to engineer the hydrochars made by hydrothermal carbonization (HTC) for phosphorous and nitrogen adsorption and pesticide absorption. The distinction here is made between adsorption and absorption. For phosphorous binding the mechanism is believed to be a surface phenomenon with binding or precipitation through the metal oxide linkage. For binding of organics the mechanism is thought to be actual surface absorption in a manner similar to a sponge taking up water. Absorption is not dependent on the metal oxide linkage.

1) Direct addition of the metal oxides before HTC, and from our preliminary experiments, metal oxides that will be investigated include CaO, MgO, ZrO_2, and La_2O_3. **(possible 20 experimental combinations)**

2) Addition of the metal chloride to the substrate, followed by hydroxide to generate the metal oxide or hydroxide *in situ*. This approach will be examined only with glucose, whey, and condensed distiller's solubles (CDS). The manure materials contain significant levels of insoluble metal phosphates, and HTC will need to be conducted at low pH to obtain a salt-free hydrochar. These materials may be useful as sorbents and as possible phosphate binding materials with post-thermal treatment **(possible 12 experimental combinations).**

3) Investigate the organic solute absorption behaviors of solvent- and acid-washed hydrochars from glucose, whey, swine manure, and cow manure; CDS hydrochar has already been evaluated. These constructs will not necessarily contain metal oxides. **(4 experimental combinations)**

Binding experiments will first focus on the creation of phosphate sorption isotherms for candidate hydrochars. The generation of an isotherm involves plotting equilibrium phosphate concentration of the substrate (a given metal oxide modified hydrochar) versus the corresponding equilibrium phosphate concentration of the bulk liquid at a constant temperature. Following the creation of a sorption isotherm, the data can be fit to various sorption models such as he Langmuir isotherm model that is commonly used.
Binding experiments for pesticides will be conducted under activity 4.

ACTIVITY 1
Summary Budget Information for Activity 1:

ENRTF Budget:	**$ 146,900**
Amount Spent:	**$ 0**
Balance:	**$ 146,900**

Outcome	**Completion Date**
1. *Identification of best combinations of biomass source and metal oxide for adsorption of phosphorous and nitrogen Construct sorption isotherms for best candidates. This will require the manufacture and testing of approximately 100 samples in this first round evaluation.*	July 30, 2016
2. *Conduct statistically designed experiments to optimize HTC process conditions for "best" candidates. Responses will be equilibrium absorption and surface area of heat-modified sample integrated with results from the Spokas lab as indicated in Activity 2.In an iterative fashion. One statistically designed experiment requires a minimum of 11 experiments to consider 3 independent variables (time, temperature and concentration of solid). If there were 4 "best" candidates from the starting array of 36 combinations then 44 experiments would be conducted.*	January 31, 2017
3. *Determine costs associated with producing "best" hyrochar candidates considering variables such as biomass cost, HTC yield, metal additive cost and post treatment costs*	January 31, 2017
4. In collaboration with the Spokas and Rice labs, provide hydrochar samples for evaluation as pesticide absorbents. **The number of samples will be at least 15 at the outset and an additional 11 for each candidate that survives the initial screening.**	June 30, 2017

Activity Status as of *[Dec. 31, 2015]***:**

Activity Status as of *[July 30, 2016]***:**

Activity Status as of *[Dec.31, 2016]***:**]**:**

Final Report Summary: July 31, 2017

ACTIVITY 2: Characterization of Hydrochars (those produced in Activity 1).

Description: Hydrochars will be evaluated for total C, total N, GHG (green house gas) impacts (result of adding hydrochar to soil) including mineralization potential of hydrochar along with impact on total soil microbial biomass.

Hydrochars will be characterized for the sorbed volatile contents both through headspace thermal desorption and solvent extraction techniques to evaluate the impact of production conditions on the resulting sorbed volatile components as well as %C, %N, surface area, moisture content, volatile content, and fixed carbon.

The saturated hydraulic conductivity (K_{sat}) will be measured with the KSat equipment in the University laboratory

Soils will be collected from various depths and landscape positions from different fields in Minnesota to obtain soils with a variety of physical, chemical, and biological properties. Soils will be selected based on their percent organic carbon content, clay content, and soil pH.

Summary Budget Information for Activity 2: **ENRTF Budget: $ 48,375**
Amount Spent: $ 0
Balance: $ 48,375

Outcome	Completion Date
1. Characterization of 100+ samples of hydrochar from various biomass sources and under varying processing conditions as provided from Activity 1. Characterization includes total C and N, mineralization potential of hydrochar along with impact on total soil microbial biomass and hydraulic conductivity. We will also conduct further surface characterization of these materials through scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX) analyses and FTIR (University of Minnesota – CharFac facility) to gain an understanding of the microstructure influences on the observed sorption behavior.	May 31, 2016
2. Greenhouse Gas production potential **will** be measured to assess the impact of the various types of hydrochar (conditions, feedstocks) on nitrogen processes and which have potential as an agent for improving agricultural soil nitrogen dynamics for those samples selected in the characterization studies above.	May 1, 2017

Activity Status as of *Dec.31, 2015*:

Activity Status as of *[July 30, 2016]*:

Activity Status as of *[Dec.31, 2016]*:

Final Report Summary: July 30, 2017

ACTIVITY 3: Real-time monitoring of P/NO_3 sorption. Activity starts in Jan. 2016

Description: A variety of hydrochars will be screened for their abiotic sorption properties for N and P. This initial phase will consist of a series of batch experiments to produce sorption isotherms (e.g. Langmuir or Freundlich isotherms) for the hydrochar materials produced from activity 1. Samples will be analyzed for nitrate, nitrite, ammonia, and phosphorus by colorimetric methods (Lachat QuickChem) to confirm ion specific electrode readings. The amount of P or N on the adsorbents will be calculated based on the difference between initial and final aqueous concentrations. Pearson's correlation analysis will be used to assess the modeled and observed isotherm values (R^2 and P values), and ion specific electrode data will be used for kinetic fits.

Soil P saturation indices and the calculated P Langmuir adsorption maximum (S_{max}) are used to determine the proper application rate of P to avoid over application and high leaching rates. Therefore, we will also determine the alteration in these indices as a function of hydrochar application rates to 3 different soil texture types from Minnesota (e.g., Becker sand, Waukegan silt loam, and Webster clay loam) to assess the potential use of hydrochar as an *infield* buffer strip amendment abatement strategy.

Summary Budget Information for Activity 3: **ENRTF Budget: $ 41,867**
Amount Spent: $ 0
Balance: $ 41,867

Outcome	Completion Date

1. Sorption/desorption experiments on samples selected from Activity1 with soil P saturation indices and calculated P Langmuir adsorption maximum (S_{max}) for samples of interest.	May 31, 2017
2. Determine change in indices (P saturation and S_{max}) as function of hydrochar application rates for 3 Minnesota soil types.	June 30, 2017

Activity Status as of *[July 30,2016]***:**

Activity Status as of *[Dec 31, 2016]***:**

Final Report Summary: July 30, 2017

ACTIVITY 4: Pesticide sorption
Description:
The extent of pesticide sorption on hydrochar will be evaluated in laboratory experiments conducted with both ^{14}C (radioactive labeled pesticides), ^{13}C (stable isotope labeled), and unlabeled pesticides which will be performed in batch sorption studies.

The sorption properties of the hydrochars will be evaluated for the following 4 pesticides, which are some of the most heavily used in Minnesota and representative of the major chemical classes of pesticides: Lambda-cyhalothrin (a pyrethroid), Chloropyrifos (organophosphate pesticide), Pyraclostrobin (fungicide) and Clothianidin (a neonicotinoid).

Pesticide degradation and desorption characteristics will also be determined.

Batch equilibrium experiments will be conducted to determine sorption isotherms of pesticides and their depredates on soils with dissimilar organic carbon contents, clay contents, and pH levels.
Soils will be collected from various depths and landscape positions from different fields in Minnesota to obtain soils with a variety of physical, chemical, and biological properties.

Immediately following the sorption experiments, desorption will be measured from two concentration points of the sorption isotherms (i.e. 0.04 and 0.4 ug mL^{-1}).
Determine if exhausted hydrochar containing pesticide can be safely incinerated.

Summary Budget Information for Activity 4: (start date Jan.1, 2016) **ENRTF Budget: $ 159,807**
Amount Spent: $ 0
Balance: $ 159,807

Outcome	Completion Date
1. *Sorption experiments on best candidates from activity 1 with both radioactive labeled pesticide isotopes and pesticides without a radioactive isotope.*	May 31, 2017
2. *Desorption experiments on "best" candidates from sorption studies. (start date June 1, 2016)*	May 31, 2017
3. Incineration studies with analysis of combustion exhaust gases.	May 31, 2016
4. *The amounts of pesticide and depredate sorbed to the soil in the batch equilibrium sorption-desorption studies will be calculated as the difference between the initial solution concentration and the equilibrium solution concentration of the supernatant, considering both the volume of the solution and the quantity of soil. Sorption and desorption isotherms will be calculated using the linearized form of Freundlich equation.*	June 30, 2017

Activity Status as of *[July 30, 2016]***:**

Activity Status as of *[Dec. 31, 2016]***:**

Final Report Summary: July 30, 2017

ACTIVITY 5: Simulate hydrochar sorption capacity to remove dissolved phosphorous, nitrates and pesticides from drain-tile effluents and other runoff sources by utilizing a laboratory scale flow-through column

Description:

Flow-through columns:

Figure 6. Illustration of laboratory column set-up.

Select the optimum P and NO_3 sorbing material as well as the best pesticide sorbing materials and analyze their functionality in laboratory flow-through column experiments to investigate the flow and sorbing properties of hydrochar media in a water flow situation, like tile drain flows. Variables that will be measured during the experiments include nitrate-N/PO_4 concentration, total dissolved carbon, and dissolved organic carbon concentration of the effluent, and oxidation-reduction potential and temperature within each filter. Pesticide sorption will be measure by spiking the column with a target pesticide and subsequently measuring it's concentration in the effluent. Hydraulic conductivity will be measured at the beginning and end of the experiment.

The study will be structured as a completely randomized design. A three-factor, repeated measures analysis of variance will be performed for each dependent variable, with factors treatment, temperature, and time. The experimental design calls for two 6-month runs conducted in series. Between the runs there will be some down time for emptying, cleaning, and repacking the columns.

Summary Budget Information for Activity 5: (start date Jan.1, 2016) **ENRTF Budget: $ 47,180**
Amount Spent: $ 0
Balance: $ 47,180

Outcome	Completion Date
1. *Conduct two-six month duration flow –through study for hydrochar capacity for sorption of phosphorous, nitrates and selected pesticides.*	June 30, 2017

Activity Status as of *[July 30,2016]***:**

Activity Status as of *[Dec. 31, 2016]***:**

Final Report Summary: July 30, 2017

ACTIVITY 6: Apply our understanding of how modified hydrochars work in the laboratory to the complexity of conditions that exist across the landscape and to identify gaps in information relevant to the deployment of hydrochars in the field which can guide further laboratory developments and field experiments.

Description: Develop a protocol for the use of modified hydrochars across Minnesota, summarized in a handbook on the topic. The handbook will be targeted at farmers and other land managers wishing to apply modified hydrochars to local areas. In addition the handbook will encourage the widespread interest in and use of modified hydrochars so that this technology can be developed for applications beyond the scope of the project, and agricultural deployment across the region. To achieve this information gathered from literature review, laboratory testing, and ecotoxological testing will be integrated to develop three specific objectives as detailed below.

Summary Budget Information for Activity 6: (start date Jan. 1, 2016)

ENRTF Budget: $ 60,871
Amount Spent: $ 0
Balance: $ 60,871

Outcome	Completion Date
1. Calculate the ideal size of modified hydrochar filters in order to maximize nutrient and pesticide removal from tile drain run-off without impeding the flow of water from agricultural fields.	Sept. 30, 2016
2. Examine the potential toxicity of modified hydrochars to aquatic macro invertebrates.	Dec.31, 2016
3. Develop a handbook designed to help land managers and farmers use modified hydrochars to improve aquatic ecosystem health and function while improving the quality of agricultural soils.	June 30,2017

Activity Status as of *(July30, 2016)*

Activity Status as of *[Dec.31, 2016]***:**

Final Report Summary: July 30, 2017
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V. DISSEMINATION:
Description: Status reports will be provided on a quarterly basis with the final report on July 30, 2017**.**Technical articles will be written for each of the six activity areas and submitted for publication in peer-reviewed technical journals. In addition we will develop a handbook designed to help land managers and farmers use modified hydrochars effectively and identify key areas of environmental research that need to be addressed prior to the widespread application of these modified hydrochars. In the handbook we will identify what modified hydrochar is, why it was developed, why it is an improvement over other methods of nutrient remediation, and where and when it can be used effectively.

Status as of *[July 30, 2016]***:**

Final Report Summary: July 31, 2017

VI. PROJECT BUDGET SUMMARY:

A. ENRTF Budget Overview:

Budget Category	$ Amount	Overview Explanation
Personnel:	$ 382,102	1 project manager at 50%FTE for 2 years, 1Research Scientist at 40%FTE for 1.5 years, 1 Research technician at 100%FTE for 1 year, I Grad Student (EEB) at 100%FTE for 1 year, I Grad student (Soils) at 50% FTE for 2 years, I grad student (Soils) at 37.5% FTE for 2 years,. Undergraduate student workers at6 62.5%FTE for 2 years.
Professional/Technical/Service Contracts:	$ 2000	Graphic and printing for handbook
Capital Expenditures Over %5000.	$ 32,600	Two-gallon Paar high-pressure reactor and associated controls and installation to support work on Pesticides and provide samples for other activities.
Equipment/Tools/Supplies:	$ 87,898	Supplies consumables, calibration standards, probes for nitrate, oxygen and phosphorous, analytical testing for over 200 samples of hydrochar, pesticide standards, radio labeled pesticides, liquid chromatography-mass spec analysis 100 plus pesticide samples, fittings, tubing and pump for flow through columns, Char Fac user fees, GC support gases, toxicity tests.
Travel Expenses in MN:	$ 400	Mileage for In state travel to secure various soil samples
TOTAL ENRTF BUDGET:	**$ 505,000**	

Explanation of Use of Classified Staff:

Explanation of Capital Expenditures Greater Than $5,000: Our current Paar high-pressure reactor is only I liter volume and as such limits us severely in how much hydrochar we can provide for testing. The 2-gallon reactor (8 liters) will have about 7 times the capacity of our small machine. Without the 2-gallon reactor we could not provide the hydrochar material that the other researchers need for their experiments and evaluations. For example we can make about 7 different samples of hydrochar in a week. The larger reactor would produce about 50 equivalent samples in a week. The reactor is $29,100. Installation in a hood and safety shields add about $3500. This equipment is absolutely essential. This equipment will be useful for research in this area for many years and in fact can be used by others in the University conducting high pressure research.

Number of Full-time Equivalents (FTE) Directly Funded with this ENRTF Appropriation: There are 6.6 FTE funded by this project.

Number of Full-time Equivalents (FTE) Estimated to Be Funded through Contracts with this ENRTF Appropriation: None

B. Other Funds:

Source of Funds	$ Amount Proposed	$ Amount Spent	Use of Other Funds
Non-state			

The time for Dr. Kurt Spokas, Dr. Pamela Rice, and Dr. Gary Feyereisen and their associated technicians (estimated at 5% commitment/year) is at no cost to the LCCMR project, since all are federal employees and their salary is provided through appropriated federal funding through the USDA-ARS.	$ 44,176.	$	These are in-kind funds and will be used to support the efforts of Drs. Rice, Spokas and Feyereisen
State			
	$	$	
TOTAL OTHER FUNDS:	**$ 44,176**	**$**	

VII. PROJECT STRATEGY:

A. Project Partners:

Project Partners Not Receiving Funds;

Dr. Clarence Lehman, Dept. Ecology, Handbook for engineered hydrochar field use protocol. **His** research principle is to contribute to understanding the combined physical-biological-social dynamics of the earth, to help promote its long-term habitability for ourselves and our fellow creatures, using computation and biological theory as a primary unifying theme. He is a Resident Fellow. Institute on the Environment, University of Minnesota. Was Associate Director Cedar Creek Natural History Area, University of Minnesota.

- Dr. Gary Feyereisen, Dept. Soil, Water, Climate; USDA-ARS, **Filtration of phosphorous from point sources**. He is a research agricultural engineer at the Soil and Water Management Research Unit, St. Paul, MN, who investigates nutrient transport processes and management practices designed to minimize agricultural impacts on water quality. He served as a research hydrologist at the Pasture Systems and Watershed Management Research Unit in University Park, PA, quantifying impacts of manure management strategies on hydrology and water quality and designing non-point source pollution filtration methods.
- Dr. Kurt Spokas, Dept. Soil, Water, Climate; USDA-ARS, **Phosphorous sorption/desorption of engineered hydrochars in soils**. He has a broad background in soil science. His major research areas include the impact of management practices (particularly herbicides, fungicides and biochar additions) on the cycling of carbon, nitrogen, and other greenhouse gases in agricultural systems. This includes the study of the transport and surface exchange of greenhouse gases (nitrous oxide, carbon dioxide, methane) and the impacts of seasonal cycling on their transport.
- Dr. Pamela Rice, Dept Soil, water, Climate; USDA-ARS, **Pesticide Sorption.** She is a toxicologist whose experience includes basic and applied research evaluating the fate and transport of chemicals in agricultural and non-agricultural environments, the design and assessment of mitigation and remediation strategies to reduce off-site chemical transport, evaluation of ecological impacts of agricultural and non-agricultural practices and the toxicological significance of chemical residues in the environment.

Project partners Receiving Funds:

Dr. K.J. Valentas, Adj. Professor Biotechnology Institute, P.I. and **process engineering expertise for manufacture of engineered hydrochars.** Valentas *is Adjunct Professor in the Biotechnology Institute (BTI) at the University of Minnesota. Previously he was Director of the BTI for 16 years and Associate Director for two years. Prior to joining BTI, Valentas was Sr. Vice President of Engineering at Pillsbury/Grand Met, and in total spent 24 years in industry at Sinclair Oil, General Mills and Pillsbury/Grand Met. He holds ten patents related to process engineering. Valentas is a recognized expert in process engineering and the author of two books on the subject. His research while at the BTI has focused on renewable energy with particular emphasis on thermochemical processing and hydrothermal carbonization (HTC) of biomass. ENRTF funds $103,714*

- Research Scientist (TBD) to conduct hydrothermal carbonization experiments and related research on hydrochars including post modification. ENRTF funds $76267
- Three graduate students (ENTRF funds $118,650 for three graduate students) and one research technician (ENRTF funds, $49,100) to support efforts of Valentas, Feyereisen, Spokas, Rice and Lehman.
- Undergraduate workers to support Spokas, Rice and Feyereisen (ENRTF funds of $34372 in aggregate)

B. Project Impact and Long-term Strategy:

Agricultural chemicals such a phosphorous, nitrates and pesticides that are transported by rainfall, irrigation or snow melt water to surface waters by overland runoff or through draintiles are a serious threat to our fisheries and waterways. Phosphorous and nitrogen are fertilizers for algae and other aquatic plants which often leads to oxygen depletion and eutrophication and a decline in fisheries. Pesticides in either the soil or in leachate that ends up in our waters can seriously impact fish and human consumption in drinking water. Pesticides such as the neonicotinoids have recently been implicated in the decline of the population of agriculturally important insects such as pollinating bees and immune suppression of fish. Once these chemicals enter our water resources it is virtually impossible to remove them and it is much better to prevent them from entering in the first place.

The first goal is to develop a hydrochar based material for sorption of phosphorous and possibly nitrogen from drainage waters, which ideally will then be able to be recycled as a soil amendment following its exhaustion. In this fashion, the sorbed nutrients can be reapplied to the field, which will reduce agronomic input costs, improve environmental sustainability, be beneficial to the soil microbial community and improve potential adoption by farmers/land owners.

The second goal is to design a hydrochar material specifically to absorb pesticides commonly used in agricultural operations in either point source or distributed applications.

Success on this project would be a significant positive step for the mitigation of pesticide, phosphorous and possibly nitrate pollution of Minnesota's waters. The process for making the engineered hydrochars is expected to be patentable by the university and any royalties would be shared with the ENRTF. Future funding for development and ultimate commercialization would likely be a new start-up or collaboration with Minnesota companies such as 3M, Donaldson, Cargill, etc. who are active in water treatment and/or agriculture.

C. Funding History:

Funding Source and Use of Funds	Funding Timeframe	$ Amount
Minnesota Corn Growers/ AURI/ IREE, "Recovering Valuable Bio-based Products from Thin Stillage in Corn Ethanol Plants.	4/25/2013 to 12/31/2014	$ 109,700

Minnesota Corn Growers, "Converting Distillers Solubles to Slow Release Fertilizers and Adsorbents for Phosphorous. "	3/31/2014 to 6/30/2015	$ 97,000
		$

VIII. FEE TITLE ACQUISITION/CONSERVATION EASEMENT/RESTORATION REQUIREMENTS: N/A

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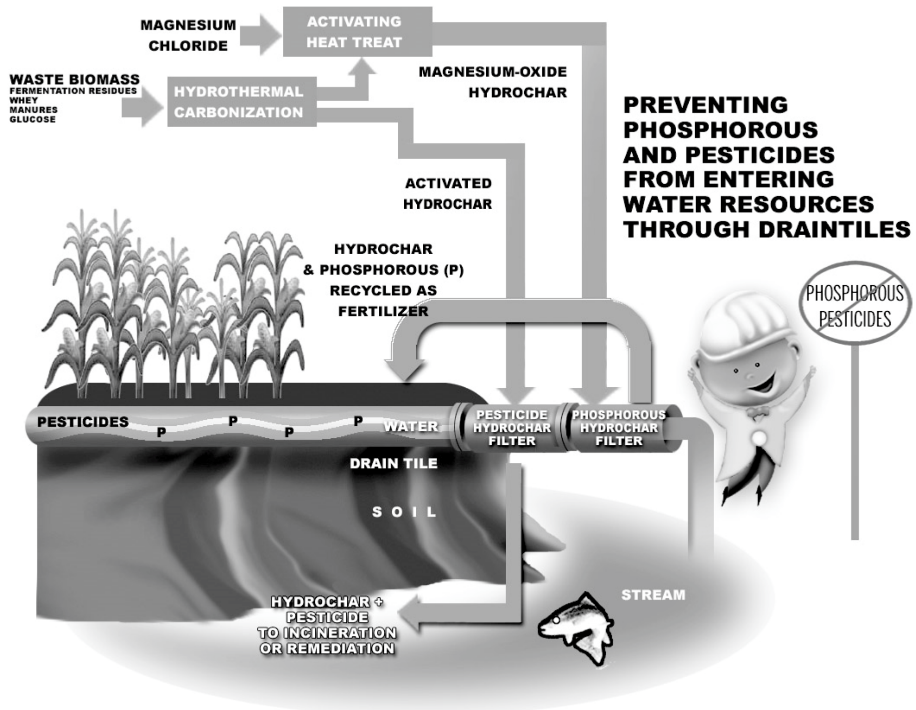

X. RESEARCH ADDENDUM: Submitted as separate document.

XI. REPORTING REQUIREMENTS:

Periodic work plan status update reports will be submitted no later than *(Dec. 31, 2015*], [*July 30, 2016*], and [*Dec. 31, 2016*]. A final report and associated products will be submitted between June 30 and August 15, 2017.

Environment and Natural Resources Trust Fund

M.L. 2015 Project Budget

Project Title: Preventing Phosphorous and Pesticides from Entering Water Resources Through Draintiles

Legal Citation: *Fill in your project's legal citation from the appropriation language - this will occur after the 2015 legislative session.*

Project Manager: Kenneth J. Valentas

Organization: University of Minnesota

M.L. 2015 ENRTF Appropriation: $*505,000-*

Project Length and Completion Date: 2 years , June 30, 2017

Date of Report: 10/15/2014

ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Activity 1 Budget	Amount Spent	Activity 1 Balance	Activity 2 Budget	Amount Spent	Activity 2 Balance	Activity 3 Budget	Amount Spent	Activity 3 Balance	Activity 4 Budget	Amount Spent	Activity 4 Balance	Activity 5 Budget	Amount Spent	Activity 5 Balance	Activity 6 Budget	Amount Spent	Activity 6 Balance	Total Budget	TOTAL BALANCE
BUDGET ITEM	*Make & evaluate hydrochars*			*Characterize hydrochars*			*Real time monitor P/NO3*			*Pesticide sorption*			*Flow through column*			*Handbook and scale-up*				
Personnel (Wages and Benefits) Overall	$128,131		$128,131	$34,633		$34,633	$34,737		$34,737	$88,297		$88,297	$41,435		$41,435	$54,871		$54,871	$382,104	$382,104
Ken Valentas, P.I. , Biotechnology Institute, overall technical director, grad. Student supervision, process engineering, $103,714 (92.5% salary, 7.5% fringe),0.5 FTE for two																				
TBD Biotechnology Institute Research Associate, Conduct and supervise hydrothermal carbonization/hydrochar experiments, $76,267 (92.5% salary, 7.5%																				
Research technician,TBN, $49,100 (78.6% salary, 21.4% fringe)100% for one year =																				
Grad. Student, EEB Dept. TBN, $44,500, (52.1 % salary, 47.6% fringe), 100% for I year = 1 FTE																				
Grad student(PhD),, TBN, Soils Dept. $40325 (55.3% salary, 47.9% fringe), 50% for 2 years =																				
Grad student (MS), TBN,Soils Dept., $33824, (49.5%salary, 50.5% fringe), 37.5% for two years = 0.75 FTE																				
Undergraduate student workers; 25 hrs./week x104 weeks = 1.25FTE ; 2600 hrs. @ $13.22/hr $34372. (no fringe)																				
Professional/Technical/Service Contracts																				
Handbook preparation (graphics and typing)																				
Equipment/Tools/Supplies																$2,000		$2,000	$2,000	$2,000
Analysis and testing for phosphorous, nitrates, carbon content, surface area(SEM),																				
Char Fac user fees $50/hr. x 300 hrs.	$16,519		$16,519	$780		$780													$17,299	$17,299
Probes for nitrate, dissolved oxygen, pH				$10,000		$10,000	$5,000		$5,000										$15,000	$15,000
PVC Fittings and tubing for flow through column and calibration standards				$2,632		$2,632	$2,000		$2,000										$4,632	$4,632
Consumable supplies													$2,745		$2,745				$2,745	$2,745
Pesticide standards, centrifuge tubes	$2,250		$2,250	$330		$330	$130		$130	$4,000		$4,000							$6,710	$6,710
Radio labelled pesticides										$8,110		$8,110							$8,110	$8,110
GC analytical column										$10,000		$10,000							$10,000	$10,000
LC-Mass Spec 100 samples x $120										$1,400		$1,400							$1,400	$1,400
Toxicity testing										$12,000		$12,000							$12,000	$12,000
Pump for flow through column																$4,000		$4,000	$4,000	$4,000
Capital Expenditures Over $5,000													$3,000		$3,000				$3,000	$3,000
Par hi pressure reactor for making hydrochar to support project and especially activity 4 (pesticides) , reactor is $29,100 and installation with safety equipment is estimated at																				
Printing of users handbook										$32,600		$32,600							$32,600	$32,600
Open access publication for public dissemination of technical research results										$3,000		$3,000							$3,000	$3,000
Travel expenses in Minnesota																				
in state travel to secure soil sample, aquatic samples and the like. Anticipated mileage										$400		$400							$400	$400
COLUMN TOTAL	**$146,900**	**$0**	**$146,900**	**$48,375**	**$0**	**$48,375**	**$41,867**	**$0**	**$41,867**	**$159,807**	**$0**	**$159,807**	**$47,180**	**$0**	**$47,180**	**$60,871**	**$0**	**$60,871**	**$505,000**	**$505,000**