Environment and Natural Resources Trust Fund
2018 Request for Proposals (RFP)

Project Title: **ENRTF ID: 051-B**

Hydrochars to Remove Nitrates from Agricultural Drainage

Category: B. Water Resources

Total Project Budget: $ 359,000

Proposed Project Time Period for the Funding Requested: 2 years, July 2018 to June 2020

Summary:

A modified hydrochar that will reduce the amount of unwanted nitrates in agricultural waters and also improve agricultural sustainability through recycling the nitrate nutrients will be developed from agricultural residues.

Name: Kenneth Valentas

Sponsoring Organization: U of MN

Address: 140 Gortner Lab., 1479 Gortner Ave.

St. Paul Mn. 55108

Telephone Number: (763) 595-0365

Email valentas@umn.edu

Web Address

Location

Region: Statewide

County Name: Statewide

City / Township: Statewide

Alternate Text for Visual:

none

_____ Funding Priorities	_____ Multiple Benefits	_____ Outcomes	_____ Knowledge Base
_____ Extent of Impact	_____ Innovation	_____ Scientific/Tech Basis	_____ Urgency
_____ Capacity Readiness	_____ Leverage	_____ TOTAL	_____%

PROJECT TITLE: Hydrochars to Remove Nitrates from Agricultural Drainage

I. PROJECT STATEMENT

Nitrate is a widespread water contaminant in streams, rivers, lakes and groundwater that is a threat to human health and contributes to eutrophication of our groundwater resources. Nitrate levels in surface waters in Minnesota exceeded 5 ppm (mg/L) at 41% of the monitored sites across the States from 2000-2010, with a combination of transport and application rates/timings directly influencing nitrate movement from agricultural systems to surface waters. Nitrate does not readily bind to the soil and is highly susceptible to leaching. (In our current LCCMR project we have had success in developing hydrochars that will absorb phosphorous and certain pesticides from water at concentrations typical of agricultural drainage. However as expected, nitrate removal from water has been a challenging task. But recently **we have found an innovative means to construct modified hydrochars from readily available agricultural residues that capture nitrates from agricultural waters. These nitrates could potentially then be recycled back to the land.**
Chemical and physicochemical methods for nitrate removal tend to be expensive and not readily applicable in agricultural situations. Biological denitrification reactors can remove nitrates but do so by conversion into N2 gas, negating any potential re-use of the lost nutrient value. Conversely, adsorption technology has the advantages of simplicity of use and a relatively low cost, at least for water treatment applications for removal of various pollutants. Activated carbons or ion exchange resins are utilized in water treatment plants and in-home filtration systems for nitrate removal. Designed modification of carbon surfaces to enhance their sorption capacity is one way to develop a new material that can adsorb more than the current commercially available products and increase sustainability through the re-use of the sorbed nutrients. **In preliminary experiments, we have developed one such candidate material created through the hydrothermal carbonization of corn stover. This hydrochar was found to possess a nitrate sorption capacity comparable to a commercially available expensive activated carbon (Filtrasorb 400). However, we believe more can be done to achieve an even higher sorption capacity and achieve a very promising solution for Minnesota Agriculture.**
Our current LCCMR project which is focused primarily on phosphorous and pesticide removal from agricultural waters will be essentially completed by June 30, 2018. However, our work on nitrate removal, while very promising, is at the very early stage of development and requires a substantial effort to increase nitrate sorption of the hydrochar to levels that would be meaningful for agricultural drainage applications.
For this new proposal the overall goal is:

Overall Goal:
Develop an optimized material that will reduce the amount of unwanted nitrates in agricultural waters and at the same time improve agricultural sustainability through recycling the nutrients that otherwise would have been transported down the Mississippi.

Outcomes.
(1) A customized material that will adsorb nitrates (> 10 mg/g) from agricultural drain-tile water,
(2) A modified hydrochar that could also be used in a buffer strip along waterways or incorporated in the field as an amendment to reduce nutrient leaching and losses.
(3) A hydrochar material that could be used as a soil amendment that can be recycled as a slow release fertilizer to reduce loss of nutrients through leaching

II. PROJECT ACTIVITIES AND OUTCOMES

Activity 1: Make and evaluate modified hydrochars for nitrate sorption. Chars will be modified with various activating agents and subjected to post thermal treatment and evaluated for nitrate sorption as measured with a Hach spectrophotometer with a minimum sorption target of > 10 mg/gram of char. Surface area and pore volume distribution will be measured by BET analysis or alternative. Active chemical moieties will be characterized by FTIR analysis. **Budget: $ 150,000**

Outcome	Completion Date
1. Test hydrochars made from various biomass sources (corn stover, manures, fermentation residues and other agricultural residues) and activating agents for sorption from 10-20 ppm nitrate solution typical of draintile and leachate waters.	June 2019
2. Investigate chemical modification of selected hydrochars for enhanced nitrate sorption through addition of active chemical entities with an affinity for nitrates.	July 2019

Activity 2: Characterize nitrate sorption properties of "best" modified hydrochars. Equilibrium Isotherms and sorption kinetics will be determined experimentally. **Budget: $ 110,000**

Outcome	Completion Date
1. Develop sorption/desorption isotherms for best hydrochars .	Sept. 2019
2. Evaluate sorption/desorption kinetics for best hydrochars.	Nov. 2019
3. Measure sorption capacity of best hydrochars in breakthrough column tests.	March 2020

Activity 3: Evaluate selected hydrochars as soil amendments and fertilizer **Budget: $ 99,000**

Outcome	Completion Date
1. Determine hydrochar amendment impact on soil carbon dynamics.	April 2020
2. Assess impact on corn growth and soil properties of selected modified hydrochars.	June 2020

III. PROJECT STRATEGY

A. Project Team/Partners

Project partners Receiving Funds:

Dr. K.J. Valentas, Adj. Professor Biotechnology Institute, P.I. and process engineering expertise for manufacture of modified hydrochars.

Project partners not receiving funds:

Dr. Kurt Spokas, Dept. Soil, Water, Climate; USDA-ARS, Nitrate sorption/desorption of hydrochars in soils.

B. Project Impact and Long-Term Strategy

Success of this project would be a significant positive step towards a mitigation tool for nitrate pollution of Minnesota's waters, as well as improving the overall sustainability and environmental footprint of agricultural production.

C. Timeline Requirements

This is a two- year project that is sequential in nature and also involves lab and greenhouse scale growth and soil leaching trials.

2018 Detailed Project Budget

Hydrochar for removing nitrates from agricultural waters

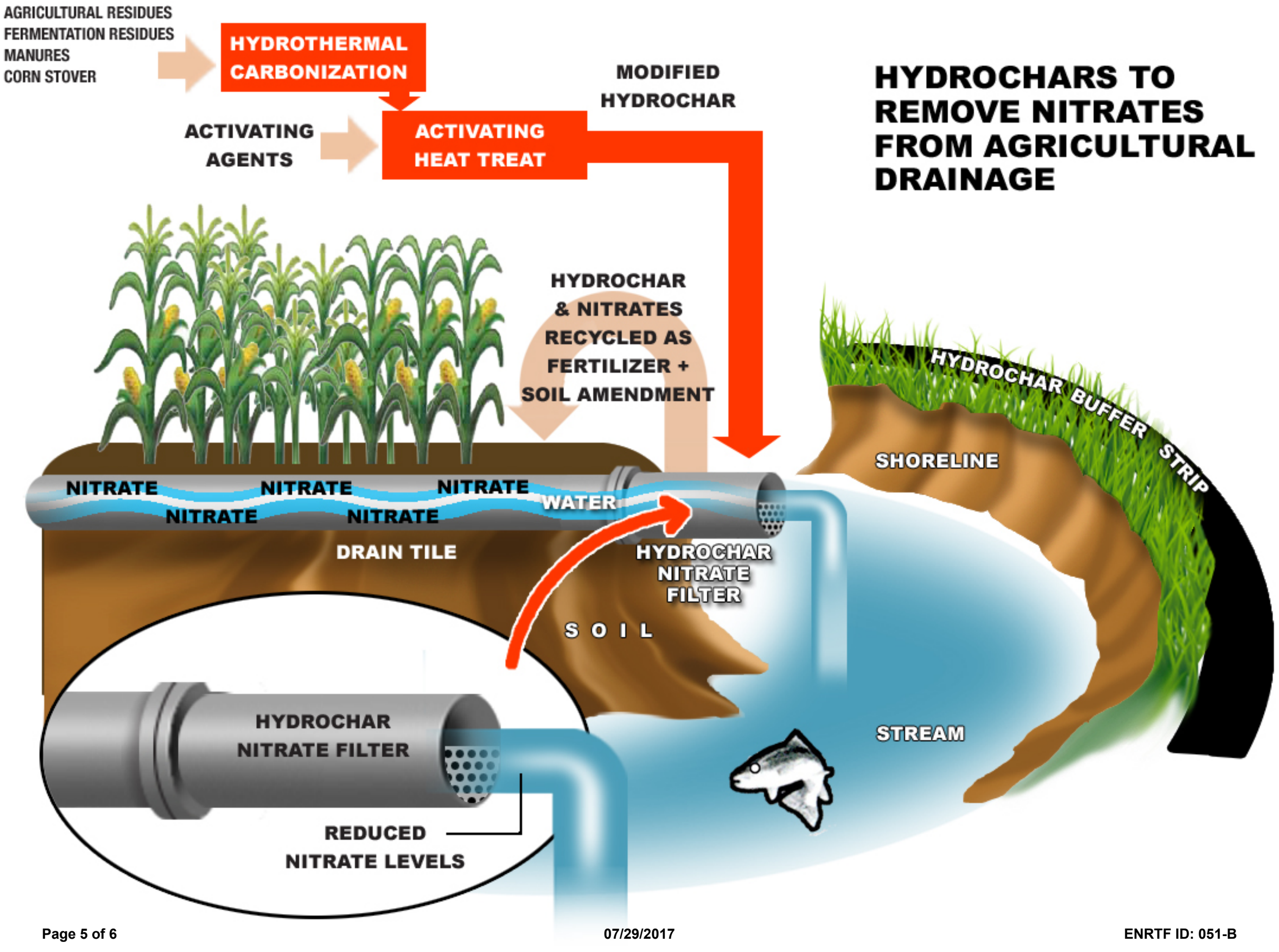
IV. TOTAL ENRTF REQUEST BUDGET *[2]* **years**

BUDGET ITEM	AMOUNT
Personnel: Ken Valentas, Adjunct Professor, Biotechnology Institute, P.I. and project manager, 37% FTE for 2 years, $100,000, 33.5% fringe, 66.5%salary. Valentas has a 50% unpaid appointment and is on soft money.	**$100,000**
Researh Technician (to be named) conduct hydrochar modification experiments and supervise analytical testing 100% FTE for 2 years $132,000, 27.2% fring, 72.8% salary.	**$132,000**
Undergraduate Student Workers. Assist in experiments and analysis for two years, $50,000, 100% salary	**$50,000**
Graduate Student (to be named). Conduct experiments on sorption capacity and soil carbon dynamics, 100% FTE for one year, $45,000, 42% fringe, 58% salary.	$45,000
Equipment/Tools/Supplies: Materials to construct breakthrough columns;Rigid tubing, connectors, stands, peristaltic pump, flow splitter	$3,500
Specialty chemical activating agents, filter papers, centrifuge tubes, glassware, gloves 12 months @ $350/month	$4,200
Supplis for anaerobic digestion tests: Gas sample bags ($5/bag x 30 bags = $1350), Syringe tips, glass vials for GC analysis ($1650)	$3,000
Quartz inserts and end fittings for Tube Oven used for post treating chars 6 @ $550 each set	$3,300
Hach spectrphotometer chemicals, tips and syringes for 1000 tests @ $4/test	$4,000
Travel: In state travel to collect soil and water sample reimbursed at University rates	$2,000.00
Additional Budget Items: Ultimte and Proximate analyssis for HHV, ash,S,C,H,N volatile and fixed carbon 30 tests at $115/test	$3,450
Elemental analysis 30 samples @ $45/sample	$1,350
FTIR surface characterization 9 samples @$50/sample	$450
Fertilizer analysis; 25 samples at $70/sample	$1,750
SEM/EDX (Scanning Electron Microscope/Xray Diffraction) 20 tests @$150/test	$3,000
BET surface area and pore volume testing. 5 test at $400/test	$2,000
TOTAL ENVIRONMENT AND NATURAL RESOURCES TRUST FUND $ REQUEST =	$359,000

V. OTHER FUNDS *(This entire section must be filled out. Do not delete rows. Indicate "N/A" if row is not applicable.)*

SOURCE OF FUNDS	AMOUNT	Status
Other Non-State $ To Be Applied To Project	N/A	*N/A*
Other State $ To Be Applied To Project During Project Period:	N/A	*N/A*
In-kind Services To Be Applied To Project During Project Period: *F&A matching at 53% = $190,270*	$190,700	*pending*
Past and Current ENRTF Appropriation:. *Preventing Phosphorous and Pesticides from Entering Water Resources Through Draintiles, 2015 appropriation. Legal Citation: M.L. 2015, Chp. 76, Sec. 2, Subd. 04d , "M.L. 2016, Chapter 186, Section 2, Subdivision 18" "Carryforward: (b) The availability of the appropriations for the following projects are extended to June 30, 2018: (2) Laws 2015, chapter 76, section 2, subdivision 4, paragraph (d), Preventing Phosphorous, Nitrogen and Pesticides from Entering Water Resources through Drain Tiles.*	$505,000	$145000 remaining. End date 6/30/2018
Other Funding History:	N/A	*N/A*

HYDROCHARS TO REMOVE NITRATES FROM AGRICULTURAL DRAINAGE



Project Manager Qualifications

Kenneth 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 nine patents related to process engineering.

His PhD in Chemical Engineering is from the University of Minnesota under Regents Professor and former head Neal Amundson. 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.

As Director of the BTI and Sr. Vice President of Engineering at Pillsbury, Valentas has gained particular expertise in managing teams of inter-disciplinary researchers and engineers in complex projects. The most recent pertinent experience relevant to this proposed project was his role as principal investigator and project manager for two state funded Biofuel Feasibility Studies (1, 2). A few pertinent peer reviewed publications are listed below (3), (4), (5), (6)

Valentas will serve as *P.I.* and project manager to provide overall direction and coordinate cross-functional activities, write reports and make presentations as required.

(1) Valentas et al (2009) “White Earth Biofuels Feasibility Study”, 94pp., Funded by MNDA under Minnesota statute 48A.10.
(2) Valentas et al (2009), “Chisago, Isanti and Pine Counties Biofuels Feasibility Study”,90pp., Funded by MNDA under Minnesota Session Laws 2007 Chapter 45.
Copies of (1) and (2) are posted at www.bti.umn.edu
(3) Biomass & Bioenergy 2010, 34, 875-882; “Hydrothermal carbonization of microalgae”
(4) Applied Energy 2011, 88(10), 3286-3290; “Hydrothermal carbonization of microalgae. II. Fatty acid, char and algal nutrient products”
(5) Biomass & Bioenergy 2011, 35, 2526-2533; “Hydrothermal carbonization of distiller’s grains”
(6) Heilmann, S., J.S. Molde, J.G.Timler, B.M.Wood, A.J.Mikula, G.V.Vozhdayev, E.C.Colosky, K.A. Spokas and Kenneth Valentas, “Phosphorous Reclamation through Hydrothermal Carbonization, of Animal Manures”, Environmental Science and Technology, 2014

Organization Description

The University of Minnesota is the state’s main research and graduate teaching institution. Our university has been repeatedly ranked number-one in the nation for Ecology/Environment and Chemical Engineering, based on the citational influence of its scientific publications.