[2015] Project Abstract
For the Period Ending June 30, 2018

Overall Project Outcome and Results

Abstract

The effective production of food and fiber relies on fertilizers to provide plant nutrients and pesticides to control weeds, insects, and plant diseases that interfere with the yield and marketability of crops. In the fields, these do an important job, but when they run off into surface or groundwater they can pose a threat to water quality and raise environmental issues. The impact of pesticides on water quality' is a technically complex subject. Phosphorus, from fertilizers, is often the limiting nutrient in aquatic ecosystems and the main culprit in eutrophication. Once these chemicals enter our waters it is virtually impossible to remove them.
The objective of this research was to determine if an engineered hydrochar, fabricated from inexpensive agricultural residues, would remove phosphorous, nitrates and pesticides from agricultural drainage waters. Our early research indicated that certain metals could be incorporated into chars to remove phosphorus and nitrates from dilute solutions. Subsequently, many experiments were performed with a wide range of biomass from corn stover to manures and with various potential activating metals.
Significant outcomes:

- **Lanthanum (a transition metal) modified corn stover hydrochars have best phosphorus removal capacity in range of 25-45 mg of P/gram char from a 50ppm solution**
- **Zinc chloride modified bio-hydrochar sorbs nitrates comparably to activated carbon**
- **Lanthanum modified bio-hydrochar can simultaneously remove phosphorous and glyphosate from dilute solution.**
- **Chars will sorb pesticides if first subjected to post-thermal heat treatment (PTT) in an oxygen-free atmosphere.**
- **Dry biomass, like cornstover, can be converted directly by PTT to a biochar that will remove pesticides.**

These results provide a path forward in preserving the quality of our water resources by reducing the phosphorous, nitrates and pesticides that migrate to waterways through draintiles. The information generated here forms the basis for field trials leading ultimately to preservation of our aquatic ecosystems.

Project Results Use and Dissemination

The University has expanded the scope of the original provisional patent to include broader claims. The new provisional patent is: U.S. Provisional Application No. 62/718,705
Title: METHOD FOR REMOVING PHOSPHORUS COMPOUNDS FROM AN AQUEOUS MEDIUM, on August 14,2018

This technology was developed with trust funds from our LCCMR project and any future revenues will be shared as required.

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

Date of Report: August 17, 2018

Date of Next Status Update Report: Final Report

Date of Work Plan Approval: June 25, 2015

Project Completion Date: June 30, 2018

Does this submission include an amendment request? No

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

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Total ENRTF Project Budget:	ENRTF Appropriation:	$505,000
	Balance:	**$0.**

Legal Citation: M.L. 2015, Chp. 76, Sec. 2, Subd. 04d , "M.L. 2016, Chapter 186, Section 2, Subdivision 18"

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.
"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."

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]***:** Experiments have begun to evaluate the phosphorous adsorption capacity of the innovative specialized metal-oxide hydrochars. Initial experiments are focused on using magnesium and zinc with hydrochars made from Condensed Distillers Solubles (CDS) that are by-products generated at corn ethanol plants. Preliminary tests with 2 ppm phosphorous concentration solutions indicate zinc is more effective than magnesium at improving phosphorus sorption. The 2 ppm concentration selected is typical of agricultural run-off waters. This work will be expanded to include more biomass feedstocks such as swine, cattle and poultry manures.

To eliminate the current timing and quantity bottlenecks in the production of the various hydrochars required for our research, we are currently collecting bids and working with the UMN facilities management evaluating equipment options that will improve capacity and maintain operational safety. These activities are part of the equipment upgrade that was in the original proposal.

Although significant work has been accomplished, initial progress has been slower than our expectations due to the retirement of a key researcher. However, we have been successful in recruiting an individual with significant expertise in hydrothermal carbonization from the Zurich University of Applied Science in Switzerland. He will join us on Jan. 11, 2016.

In addition, the timing of the grant was slightly off-cycle for the hiring of graduate students on this project. Efforts are underway to recruit a highly qualified individual for the Fall term.

AMENDMENT REQUEST (03/21/2016)

A one- year, no cost extension, of the project is requested. This will move the project completion date to June 30,2018.

The project had a slow start due to the unexpected retirement of a key researcher (S.Heilmann) prior to the official start of the project. We could not begin the search process until the project was officially funded on July I, 2015. After considerable effort, over a 6 month period, we were able to identify and hire an individual (Gabriel Gerner) with significant expertise in hydrothermal carbonization from Zurich University of Applied Science. He joined the project team on Jan. 11, 2016. In addition we have experienced delay in gaining final approval for full involvement of USDA-ARS scientists and their laboratory resources. This procedural issue should be resolved within the next few months.

In spite of these delays our initial experiments have been encouraging and this requested extension should allow us to complete the project as outlined in this work plan.

"Amendment Approved: [May 31, 2016]"

Project Status as of *[July 30, 2016]***:**
All staffing issues experienced during the last period have been satisfactorily resolved and the productivity of the group is on track.

Hydrochar samples were produced from swine, cattle and poultry manures, condensed distillers solubles (CDS), corn stover and peat. Metals that were incorporated in the hydrochars in-situ included zinc, magnesium and lanthanum. Several of the produced hydrochars were post-thermally treated to increase porosity. FTIR analysis is currently being utilized to study phosphorous sorption by metal containing hydrochars. Initial results confirm that Lanthanum (La) addition prior to the HTC process (in-situ) does significantly increase phosphorous sorption capacity compared to metals such as zinc. Conversely, Lanthanum addition after the HTC process (post addition)

does not increase sorption capacity of the hydrochar as much as insitu addition. Scanning electron microscopy (SEM) confirmed that the in-situ addition of lanthanum during the HTC process results in a char with a uniform coating of La on the char surface whereas post addition of La to the HTC hydrochar does not yield a char with uniformly bound lanthanum.

To date, 33 hydrochars prepared from 7 different biomass feedstocks and various production alternatives have been initially screened via radio-labelled isotopes across the four pesticide chemical classes most commonly used in Minnesota. Initial data analysis suggests that the dependency on post-production conditioning of the hydfrochars to increase porosity appears to have a greater influence than feedstock variety. Desorption experiments have been initiated and data is currently being collected across the various HTC hydrochars.

We have found that the Parr reactor requires regular and more frequent maintenance when corrosive chemicals such as KOH, that serve as activators and processing aids, are utilized in the HTC process. Unfortunately this takes about 4 weeks and effectively shuts down the sample preparation portion of the project. To avoid this undesirable situation we are strongly considering the purchase of a second one- liter and 0.5 liter Paar reactors so that we can cycle reactors through a regular preventative maintenance program provided by Paar to maintain a safe operation without significant down-time.

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

During the last period corn stover has emerged as the preferred biomass source for continuing experiments for phosphorous capture from agricultural water run-off and draintiles. Corn stover is a readily available agricultural residue that is inexpensive, easy to handle and transport. In addition, the hydrochar from hydrothermal carbonization processing of corn stover contains negligible amounts of phosphorous so that the char is in a "native "or null state with respect to phosphorous sorption. The best results have been with Lanthanum (La) incorporated into the hydrochar utilizing an activating agent such as potassium hydroxide or sodium hydroxide. For sorption from water containing 2.5 ppm phosphorous (in the range of agricultural waters) the hydochars have a capacity of capturing 15 – 25 mg/ gram of char. The focus now is on a series of designed experiments (DOE) to determine the optimum levels of La and activating agent to maximize phosphorous capture. The objective is to maximize P capture and minimize unused La remaining in the filtrate. Isotherms for hydrochars at varying levels of Lanthanum will be utilized to determine the optimum.

Further experiments for sorption of pesticides were carried out evaluating the capacity of various hydrochars to adsorb a radio-labeled pesticide from the neonicotinoid class of pesticides, which has become an environmental concern in recent years following links to declining bee populations. For all 5 pesticide chemical classes tested, post production conditioning has a greater impact than feedstock variety on sorption capacity on an equivalent mass basis. Post production conditioning consists of heating hydrochar to high temperature in an inert gas atmosphere for a time sufficient to increase porosity and surface area by two or more orders of magnitude. A subset of hydrochars has been selected based on adsorption performance, and isotherm analysis and kinetics testing have been initiated to further advance the selection process.

Project Status as of *[July 30, 2017]***:**
Prior to conducting a set of statistically designed experiments to optimize the HTC process for hydrochar production, preliminary experiments have been executed first to provide direction in selection of appropriate ranges for the independent variables. The center point of this design, which is for stoichiometric quantities of lanthanum and KOH, has been replicated four times with consistent results with respect to char yield, pH of the filtrate and phosphate removal. Material balances are being initiated for several experiments to fully understand how the active sorbent and other components are allocated between the two phases (char and filtrate) obtained in the HTC process and as a further measure of reproducibility.

Comparative experiments were conducted to assess the difference in phosphorous removal characteristics between hydrochars with lanthanum added in-situ in the HTC reactor versus hydrochars with lanthanum externally added after the hydrochar is made in the HTC (HydroThermal Carbonization) reactor. The post added variation had a higher rate of phosphorous removal and both hydrochars were asymptotic to the same equilibrium removal capacity. Post addition offers processing, economic and environmental advantages.

The focus on Imidacloprid, a pesticide in the neonicotinoid class, has continued since the last report. Time dependent sorption capacity testing, kinetics testing, has been completed with a high performing subset of hydrochars to investigate their ability to remove Imidacloprid from water at different time scales. This testing has yielded results consistent with previous results, that a post-production thermal treatment to increase hydrochar surface area results in the highest capacity to sorb pesticides. Additionally, a preliminary set of column leaching tests was completed with the neonicotinoid pesticide Imidacloprid to evaluate hydrochar performance in conditions similar to those in a drain tile or run-off setting.

The University of Minnesota Office for Technology Commercialization has decided to move forward with a provisional patent for a hydrochar invention which can simultaneously sorb phosphate and glyphosate from water.

Project Status as of *[Dec. 31, 2017]*:

Over 25 different chars derived from diverse animal manures (cow manure; poultry manure; swine manure), agricultural residues, fermentation residues, well performing chars from P-sorption experiments and metal impregnated hydrochars were evaluated for **nitrate sorption**. Some of these modified hydrochars had a nitrate sorption capacity comparable to a commercially available but expensive activated carbon (Filtrasorb 400) in the range of 5.6 – 8.5 mg NO_3 sorbed per gm of sorbent from a 5 ppm solution typical of agricultural waters. This was reported to LCCMR in the form of a new proposal for nitrate sorption research but was not selected for funding. Further work on nitrate sorption will not be conducted on this project.

Based on phosphorous sorption tests and other considerations, detailed in activity 3, the decision was made to focus on post addition of lanthanum to the char after hydrothermal carbonization (HTC) of the biomass instead of in-situ addition during HTC of the biomass/lanthanum cocktail. Thus, the need for an extensive DOE for the in-situ method was eliminated by this decision. Instead a modified factorial DOE was conducted with reaction time and temperature as independent variables. The purpose is to assist in selecting operating conditions to maximize yield and the efficacy of subsequent treatment by anaerobic digestion (AD) for filtrate remediation.

Considerable testing was conducted to assess the **reproducibility of results** obtained from the hydrothermal carbonization of corn stover since it has emerged as the primary biomass source for the remainder of this project. Subjecting the replicated data to statistical analysis of variance clearly showed the results to be repeatable.

In addition to reproducibility between runs it is also important to be able to account for all the material before and after a run in the form of a **material balance** as well as the distribution of carbon and nitrogen between the char and filtrate. Closure of the material balance was within acceptable limits of measurement.

The **cost of producing** the most commonly utilized corn stover based chars in the project were estimated for several important product variants. These estimates were based on a corn stover cost of $90/ short ton. The cost summary by product type is:

Basic corn stover hydrochar	$0.22/lb
Post heat treated corn stover hydrochar	$0.53/lb
Post addition lanthanum hydrochar	$1.74/lb
Post heat treat, post add lanthanum hydrochar	$2.05/lb

Since the last report, experiments were conducted on the **post addition of lanthanum** to various matrices involved 21 combinations of biomass source, hydrochar source, and other support materials as well as varying chemical treatments. Phosphate sorption from a 50 ppm phosphorous test solution showed a range of 20.8 – 45.1 mg phosphorous/gm char depending primarily on whether or not the matrix was thermally treated prior to lanthanum addition as well as the chemistry of the lanthanum cocktail utilized.

Work is currently underway to determine the optimal ratio of hydrochar to lanthanum during the addition process in order to maximize lanthanum loading and phosphorus sorption efficacy. Sorption isotherms will also be determined.

Work continues to identify hydrochars with the highest capacity to remove **pesticides** from aqueous solutions, with a particular focus on the **neonicotinoid insecticide Imidacloprid**. Since the last update, preliminary surface area measurements have confirmed that post production conditioning results in a higher surface area material and a limited **small-scale column** study has been completed with selected hydrochars. The response of the hydrochars in the columns is more representative of performance in a field application versus previously completed equilibrium sorption testing. Small-scale column results for hydrochar sorption performance are consistent with equilibrium sorption results, and the best performing hydrochars have been identified. More extensive small-scale column testing will be completed along with additional analysis methods for sorption rate and maximum sorption capacity in the coming months to complete a comprehensive summary of pesticide sorption performance. Pesticide sorption results with radio-labelled Imidacloprid have been shown to be reproducible with high confidence.

With respect to glyphosate work, the university filed a provisional patent entitled, METHOD FOR REMOVING AN ORGANOPHOSPHOROUS COMPOUND FROM AN AQUEOUS MEDIUM, on Dec. 11, 2017.

Column testing

As indicated in the last activity status (July, 30, 2017), column testing is feasible only at lab scale because of scale limitations in our char production capacity. Phosphorous sorption column testing will be with a small flow column that will be utilized to measure phosphorous breakthrough to assess sorption kinetics for selected modified chars. These tests should yield scalable data. Column testing for pesticide sorption will be conducted in a column wherein a pulse of radio-labelled imidacloprid pesticide is injected in a small gravimetric flow column and the amount of pesticide captured is determined by count and subsequent calculation. For radio-labelled pesticides, that are very expensive, this gives the most accurate and scalable results concerning the kinetics of pesticide sorption.

Toxicity testing was conducted to determine if the hydrochar was acutely toxic to water life (assessed

through *Daphnia* toxicity screening), and if lanthanum modified hydrochars (in-situ and post addition) were toxic to the *Daphnia* organisms. The data suggest that the mild toxicity of the hydrochar is primarily due to the hydrothermal carbonization step, and not from the lanthanum addition itself. There are numerous potential organic acids and low weight molecular compounds that are produced during the hydrothermal carbonization treatment, but the exact chemical toxin is unknown. Further research is needed to elucidate the chemicals responsible for the toxicity observed from the char itself. This would require testing with chars receiving increasing rinse cycles to remove potential toxins and monitoring the subsequent daphnia toxicity.

Amendment Request (01/05/2018):

It is requested to re- budget by moving funds from the overall category of "equipment, tools and supplies" which includes analytical testing for phosphorous, nitrates, carbon content and toxicity testing. The funds are to be reallocated within Activities 3 and 4 from "Equipment, tools and Supplies" to "Personnel". As the project evolved it became apparent that conducting all of the necessary tests on the outside would be cost prohibitive and to do so would jeopardize the success of the project. Instead, we chose to perform the necessary tests, such as phosphorous and nitrate measurements, with a Hach Spectrophotometer that was in our possession from another project, as well as the toxicity testing with our own laboratory personnel. This also allows us to ensure the quality of the analytical results as well since we are not constrained in performing replicates for statistical analysis. The dollar amount to be moved between these categories is $30,825.

Amendment approved by LCCMR 1/11/2018

Retroactive Amendment Request   (7/14/2018)

A retroactive re-budget is requested to move some funds from the "Equipment/Tools/Supplies" category to "Personnel". The request is retroactive due to not receiving and understanding accounting details (late June, 2018) until several weeks after actual expenditures were incurred (May, 2018). As the project spending was winding down in April/May 2018 the focus was on staying on budget and no overruns. This was achieved but when the accounting details became available the shift of some spending from the "supplies" category to "personnel" was realized and is the reason for this request.

  The additional spending for personnel was necessary to complete critically important in-house tests for lanthanum removal capacity, material balances, reproducibility testing, sorption and desorption small column experiments for lanthanum and pesticides as well as toxicity testing with Daphnia. Additionally, a detailed analysis of the cost factors for manufacturing the lanthanum chars was completed and a comprehensive cost spreadsheet was developed.

The total amount to be reallocated to personnel is $10,464. In addition, the capital expenditure for the Paar reactor system that was previously charged at $29,963. needs to be corrected to $29,923 to be consistent with the University accounting records. The resulting $40 surplus will be moved to pesticide standards within the same activity (#4). The specific retroactive changes requested are:

- activity #5 move $3000 from capital to personnel
- activity #4 move $3000 from open access and $310 from travel to personnel
- activity #6 move $4000 from pump for flow through column to personnel.
- activity #3 move $154. From probes to personnel

Amendment approved by LCCMR 7/24/2018

Overall Project Outcomes and Results: July 30, 2018

III. Overall Project Outcomes and Results: Final Report July 30, 2018

Phosphorus

To determine the best combination of biomass source, metals and activating agents, over 100 different hydrochars were made and tested. The biomass sources were varied and included poultry, swine and cattle and dairy manures, CDS (condensed distillers solubles from ethanol fermentation), corn stover and peat. Corn stover herein is defined as stalks and leaves and does not include the cobs. Metals that were incorporated in the hydrochars included zinc, magnesium, iron and lanthanum. Several of the hydrochars were post-thermally treated to modify surface chemistry.

Phosphorus removal capacity was evaluated utilizing a test solution that is typical of agricultural runoff waters (typically 2 ppm). These tests showed that the zinc and magnesium constructs sorbed negligible amounts of phosphorus.

Based on numerous phosphorus sorption experiments the most promising constructs were metal oxide hydrochars constructed from corn stover with Lanthanum(La) as the active metal and either potassium hydroxide (KOH) or sodium hydroxide (NaOH) as activating agent. These resulted in the highest phosphorus equilibrium sorption, in the range of 15-30 mg/gram of hydrochar, from phosphorus solutions typical of agricultural runoff waters (2-2.5ppm).

The best method for applying lanthanum to a char substrate is by post addition after the char has been formed as opposed to in-situ addition as part of the char formation process in the reactor. Post addition minimizes Lanthanum cost, corrosion of the reactor lining and avoids remediation to avoid any discharge of lanthanum to the environment.

The cost for producing a lanthanum impregnated hydrochar is driven by the cost of lanthanum. The cost to make a hydrochar from corn stover is about $0.22/lb. Impregnating with lanthanum would bring that cost to $1.74/lb.

Nitrates

Over 25 different chars derived from diverse animal manures (cow manure; poultry manure; swine manure), agricultural residues, fermentation residues, well performing chars from P-sorption experiments and metal impregnated hydrochars were evaluated for nitrate sorption.

The best modified chars were those made from either corn stover(CS) or condensed distillers solubles(CDS) (from ethanol fermentation of corn) with post addition of zinc chloride followed by thermal treatment in the absence of oxygen. These modified hydrochars had a nitrate sorption capacity comparable to a commercially available, expensive activated carbon (Filtrasorb 400),in the

range of 5.6 – 8.5 mg NO_3 sorbed per gm of sorbent from a 5 ppm solution typical of agricultural waters.

However, our work on nitrate removal, while very promising, was at the very early stage of development and would have required a significant effort to increase nitrate sorption of the hydrochar to levels that would be meaningful for agricultural drainage applications. A proposal to do this was submitted to LCCMR in the 2017 RFP but was not selected for funding.

Budget considerations dictated a focus on phosphorous and pesticide remediation for this project.

Greenhouse Gas Impacts

The impact of the various hydrochars on the soil microbial community was assessed with greenhouse gas production incubations for raw corn stover, corn stover hydrochar and biochar and corn stover bio-hydrochar*.

> *Bio-hydrochar is a hydrochar that has been post thermally heated in an oxygen free environment.

There was a statistically significant suppression in the production of N_2O (nitrous oxide) following hydrochar additions. However, the reduction in CO_2 production was not statistically significant. The only observable difference in oxygen consumption was for the raw corn stover. These factors would suggest that the mitigation of N_2O production is stronger than the hydrochar suppression on the total microbial population

C/N Analysis

The average Carbon content of all the chars tested was 67% with a range of 61.75 -73.5%. The raw corn stover had a C value of 45.7% so the HTC process removes sufficient hydrogen and oxygen to concentrate the C rom 45.7 to 67% on average.

Surface and Microstructure Characterization of Chars

Surface area and pore volume measurements by N_2 BET measurement may not be relevant for sorption from water at ambient conditions. This is a contentious issue and one that needs more research to resolve for applications in water.

PTT(Post Thermal Treatment) of HTC chars significantly increases pore volume of the starting hydrochar. This has practical significance when applied to hydrochars made from high water content (>90%) slurries such as manures.

Properties of Lanthanum-char constructs.

Considerable effort was expended developing isotherms, kinetic curves and measuring removal capacity of various lanthanum-corn stover constructs. These were conducted with a challenge solution containing 50 ppm phosphate. The major observations were:

- Phosphorus removal ranged from 25-45 mg phosphorus /gram char
- PTT of corn stover prior to lanthanum addition doubled the removal rate over a 24 hr. period

- HTC plus PTT of corn stover prior to lanthanum addition gave similar results as simple PTT of stover
- Zeolite and BP2000 with added lanthanum removed 40.0 and 44.5 mg phosphorous/ gram of doped support respectively.

Phosphorus removal mechanism with Lanthanum.

Lanthanum is a rare earth element that is particularly effective in sequestering phosphates from aqueous solution by forming a highly insoluble precipitate, lanthanum phosphate.
The challenge is to present the lanthanum to phosphate containing waters in a matrix that will effectively remove phosphate and have a relatively high holding capacity for phosphate. At the same time the matrix should be stable and retain the lanthanum phosphate for subsequent recovery and recycle of both lanthanum and phosphate.
Lanthanum is "attached" to or coated onto the char carrier as lanthanum hydroxide. When it is contacted by water containing phosphates it forms a highly insoluble precipitate of lanthanum phosphate. This situation raises two questions.

1.**How tenaciously does lanthanum hydroxide adhere to the char?** Does it get leached from the char carrier when exposed to water flowing in the draintile?

2. **Does the insoluble lanthanum phosphate stay "attached" to the** char carrier or is it released to the water stream?

Leaching tests showed that < 3% of the lanthanum hydroxide was lost over a 24hr. period. It is expected that this 3% loss will not increase very much for longer times as it is suspected that what is leached from the coated carrier represents lanthanum hydroxide that is loosely bound since the leaching is due to hydrodynamic friction at the water-solid interface rather than some sort of equilibrium relationship. Any lanthanum hydroxide in the tile water will come in contact with phosphate and be removed from the stream as a highly insoluble precipitate of lanthanum phosphate becoming biologically inactive.

Tests were also conducted several times to determine **if any significant amount of lanthanum phosphate was released by the char** into the water phase. **Results from an outside testing laboratory and our internal measurements with a Hach Spectrophotometer indicated amounts of <1ppm. The lanthanum phosphate appears to be tenaciously held in place by the char carrier. The mechanism by which it is bound to the char is not clear.**

Pesticide Removal/sorption

The objective of this research was to determine if an engineered hydrochar, fabricated from inexpensive agricultural residues, would remove pesticides from agricultural drainage waters. Pesticides include chemicals such as insecticides, herbicides, fungicides and others. In this study the effort was focused on herbicides and insecticides that are frequently used in Minnesota.

The propensity of materials, including hydrochar and biochar, to remove pesticides from water was determined by monitoring their concentration in solution during controlled experiments. Radiolabeled pesticide chemicals were utilized in order to precisely measure the concentration of pesticide in water. Starting concentrations and final concentrations which were used as described above were obtained by employing a liquid scintillation counter in conjunction with the radiolabeled pesticides.

From these screening experiments, it was observed that for all 5 pesticide chemical classes tested, post production thermal treatment(PTT) of the sorbent material has a greater impact than feedstock (biomass) variety on sorption capacity on an equivalent mass basis. PTT consists of heating hydrochar or solid biomass material to high temperature ($\sim 600^0$C) in an inert gas atmosphere for a time sufficient to modify the surface chemistry. It is not clear whether this actually increases the char surface area or modifies the functional groups affecting surface chemistry. But regardless, PTT changes the char or biomass in such a way as to render it more likely to sorb organic chemicals such as pesticides.

Note that there remains significant uncertainty of the particular mechanism responsible for the observed ability of modified hydrochar and biochar materials to remove pesticides from water. Our results do not closely follow established sorption models. Therefore, it cannot be concluded that the materials remove pesticides from water by way of sorption.

Glyphosate

Glyphosate is an organophosphate compound, which is used as a non-selective herbicide in agriculture. Concern about potential harmful effects of glyphosate on humans and wildlife has been increasing. Tests were conducted to determine if a lanthanum modified hydrochar designed for phosphate sorption could simultaneously adsorb the herbicide glyphosate, an organophosphate. A significant concern is that the capacity of a biochar or hydrochar to sorb glyphosate from water will be significantly reduced through competitive sorption of phosphate which might also be present in the water. The experiments yielded the surprising result that the lanthanum modified hydrochar could sorb a significant amount of glyphosate from the solution, and that the presence of excess phosphate resulted in only a small reduction in sorption capacity. Based on previous research it would be expected that the excess phosphate in solution would replace the glyphosate and reduce the glyphosate sorption to zero. That was not the result in this experiment, which indicates that the mechanism of glyphosate sorption is simultaneous and essentially non-competitive with phosphate sorption. The Office for Technology Commercialization of the University of Minnesota has filed a provisional patent. entitled, **METHOD FOR REMOVING PHOSPHORUS COMPOUNDS FROM AN AQUEOUS MEDIUM.**

Neonicotinoid Pesticides

Since radio-labelled pesticides are quite expensive and the testing of pesticide sorption is time consuming, the number of pesticides considered for more in-depth testing needed to be reduced to a reasonable number. **Glyphosate was one** of those selected because of its wide use in Minnesota agriculture. The other was **imidacloprid, a neonicotinoid** pesticide of interest. The neonicotinoid class has become an environmental concern in recent years following alleged links to declining bee populations.

A small- scale column sorption test was run with 4 chars and a sand control to gather sorption and desorption data in a flow through scenario. The results are shown graphically in Figure 1.

Figure 1. Pesticide removal by various chars
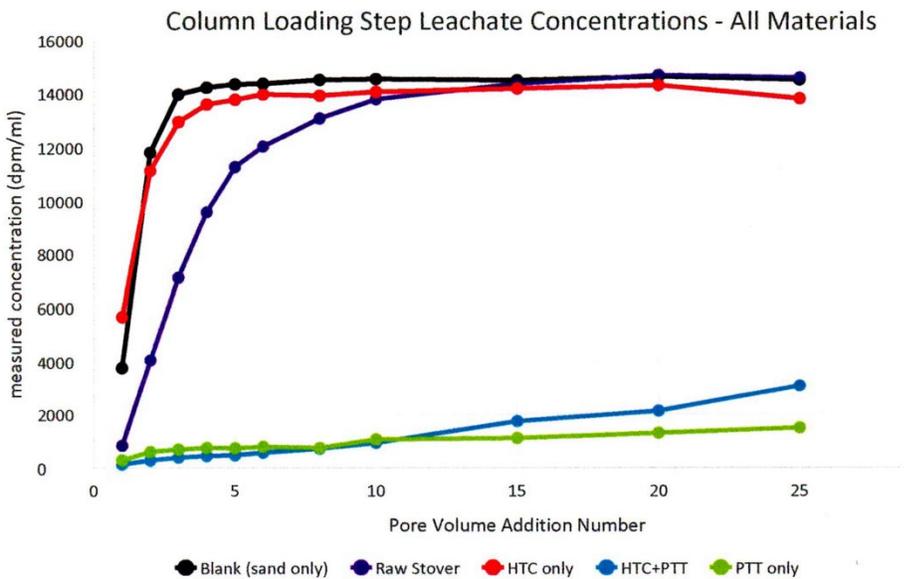
Column Loading Step Leachate Concentrations - All Materials

It was found that with this test method the raw corn stover and the stover treated only by HTC did not retain any imidacloprid after the "phase 2" rinsing steps as detailed in the procedure. Alternatively, the two materials which underwent PTT were able to each retain approximately 200ug imidacloprid per gram of material. This reinforces the importance of surface modification of the biomass or hydrochar to achieve sorption of the pesticide. It is also clear, that for a dry biomass source hydrothermal carbonization prior to PTT, is usually not necessary.

The test results for **desorption** are problematic in that some "hot" pesticide was detected for the duration of the 25 cycles in the test. There are two possible explanations for this observed desorption.

1. The chars desorb some pesticide continuously
2. The chars are known to exhibit some attrition and in so doing could be carrying char with sorbed pesticide with the particulates flowing out of the column.

It is not clear if either one or both of these phenomena are being observed. Large scale column testing would be necessary to determine if actual desorption is occurring. This requires experimentation at a considerably larger scale than bench testing in the laboratory which in turn entails equipment for making larger batches of char and larger post thermal treatment ovens as well as pelletizing equipment to compact the char in a form suitable for large column testing that will not be subject to attrition as water flows through the column or filter. Large column testing is well beyond the scope of this project.

Potential toxicity of modified hydrochars to aquatic macro invertebrates.

Toxicity screening conducted to determine if the hydrochar was acutely toxic to water life (assessed through *Daphnia* toxicity screening), and if lanthanum modified hydrochars (in-situ and post addition) were toxic to the *Daphnia* organisms.

To summarize, the data suggest that the toxicity of the hydrochar is primarily due to the hydrothermal carbonization step, and not from the lanthanum addition itself. There are numerous potential organic acids and low weight molecular compounds that are produced during the hydrothermal carbonization treatment, but the exact chemical toxin is unknown. This would be supported by the lower numerical results in the post-La addition, since this hydrochar would be rinsed again during this post-lanthanum addition and thus reduce the concentration of potential toxins emanating from the char itself. This also implies that more thorough rinsing of the hydrochar to remove more of the organics of the interstitial liquid held loosely by the char would reduce the toxicity. Since the recommended method for lanthanum incorporation is by post addition it is important to note that the lanthanum attached to the char in this manner was not found to be toxic. More thorough rinsing of the char prior to lanthanum addition should prove beneficial.

Abstract

The effective production of food and fiber relies on fertilizers to provide plant nutrients and pesticides to control weeds, insects, and plant diseases that interfere with the yield and marketability of crops. In the fields, these do an important job, but when they run off into surface or groundwater they can pose a threat to water quality and raise environmental issues. The impact of pesticides on water quality' is a technically complex subject. Phosphorus, from fertilizers, is often the limiting nutrient in aquatic ecosystems and the main culprit in eutrophication. Once these chemicals enter our waters it is virtually impossible to remove them.

The objective of this research was to determine if an engineered hydrochar, fabricated from inexpensive agricultural residues, would remove phosphorous, nitrates and pesticides from agricultural drainage waters. Our early research indicated that certain metals could be incorporated into chars to remove phosphorus and nitrates from dilute solutions. Subsequently, many experiments were performed with a wide range of biomass from corn stover to manures and with various potential activating metals.

Significant outcomes:

- **Lanthanum (a transition metal) modified corn stover hydrochars have best phosphorus removal capacity in range of 25-45 mg of P/gram char from a 50ppm solution**
- **Zinc chloride modified bio-hydrochar sorbs nitrates comparably to activated carbon**
- **Lanthanum modified bio-hydrochar can simultaneously remove phosphorous and glyphosate from dilute solution.**
- **Chars will sorb pesticides if first subjected to post-thermal heat treatment (PTT) in an oxygen-free atmosphere.**
- **Dry biomass, like cornstover, can be converted directly by PTT to a biochar that will remove pesticides.**

These results provide a path forward in preserving the quality of our water resources by reducing the phosphorous, nitrates and pesticides that migrate to waterways through draintiles. The information generated here forms the basis for field trials leading ultimately to preservation of our aquatic ecosystems.

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: $ 146,900
                                                             Balance: $ 0

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 30,2017
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 31,2018

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, 2018
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, 2018

Activity Status as of *[Dec. 31, 2015]***:** The majority of the work on this project has been focused on Activity 1 during the past period. Progress has been slower than anticipated due to the retirement of a key researcher (S. Heilmann). Since his retirement we have been successful in locating a highly qualified replacement (G. Gerner) who recently completed a Masters degree at Zurich University of Applied Sciences, Wadenswill, Switzeland. He has demonstrated expertise in hydrothermal carbonization processes that are central to our research program. Gerner will begin work on Jan.11, 2016. This represents a 6 -month gap or delay in staffing. Due to the fact that, Mr. Gerner was a visiting scientist here at the Biotechnology Institute in mid-2014, we expect him to quickly adapt and contribute to the project.

Initial experiments have focused on hydrochars prepared from condensed distillers solubles (CDS) obtained from the stillage generated in the manufacture of corn ethanol. Metal oxide hydrochars were constructed by post-heat treatment of hydrochar with magnesium chloride and zinc chloride, separately, to determine if there are differences in phosphorous sorption by the different metals. Other researchers have reported that magnesium oxide biochars will adsorb substantial amounts (69%) of phosphorous from an 80 ppm P-solution. We confirmed these results, but rather are interested in evaluating performance with a test solution that is more typical of agricultural runoff waters (typically 2 ppm). The sorption studies showed that the zinc and magnesium constructs sorbed 1000 mg/kg char and 340mg/kg respectively from a 2 ppm phosphorous challenge solution. The starting hydrochar without metal addition or post heat treatment had no detectable sorptive capacity for phosphorous from a 2ppm solution.

Capital expenditures: Our current Paar high-pressure reactor is only I liter volume and as such limits us in how much hydrochar we can provide for testing in a timely and statistically sound manner. We had originally thought that a 2-gallon reactor (8 liters) would be a significant improvement in char production capacity. However, the concern for operator and laboratory staff safety dictates that the reactor be operated in a fume hood. Unfortunately, a 2 -gallon reactor will not fit in any fume hood and it is much too expensive to construct a fume hood facility exclusively for this project. We are pursuing an option where will we still double our current capacity with a 2 -liter Parr reactor that will fit within our existing fume hood. To remain in budget for the equipment in the original proposal, we intend to proceed with the acquisition of a 2-liter Parr reactor system. However, before this occurs we will exhaust all possible walk-in hood locations for the larger 2-gallon reactor within the University.

Activity Status as of *[July 30, 2016]***:**
During this period, a total of 30 different hydrochars were produced. The biomass sources were varied and included poultry, swine and cattle manures, CDS, corn stover and peat. Metals that were incorporated in the hydrochars in-situ included zinc, magnesium and lanthanum. Several of the produced hydrochars were post-thermally treated to increase porosity. Results of phosphorous sorption tests are presented in Activity 4). Many of these samples were utilized for the analyses detailed below in the following activities.

A detailed assessment of the physical accommodation of a 2 -liter Parr reactor in standard sized hoods indicates that it is not feasible because of the vertical dimension of the reactor package. Additionally we have found that the Parr reactor requires regular and more frequent maintenance when corrosive chemicals such as KOH are utilized in the HTC process. The issue is premature failure of the rupture disc that is in place to prevent dangerously high overpressure from occurring when the reactor is operating. Since safety is of prime concern and since we will undoubtedly continue evaluating various chemicals such as KOH as activators and processing

aids we will need to have more frequent preventative maintenance procedures performed by Paar to ensure safe operation. Unfortunately this takes about 4 weeks and effectively shuts down the sample preparation portion of the project. To avoid this undesirable situation we are strongly considering the purchase of duplicate 0.5 and 1 liter Paar reactors so that we can cycle reactors through a regular preventative maintenance program provided by Paar to maintain a safe operation without significant down-time.

Activity Status as of *[Dec.31, 2016]***:**
Phosphorous sorption experiments have shown that metal oxide hydrochars constructed from corn stover with Lanthanum(La) as the active metal and Potassium Hydroxide (KOH) or Sodium Hydroxide (NaOH) as activating agent result in the highest phosphorous sorption from phosphorous solutions typical of agricultural runoff waters (2-2.5ppm). Corn stover is an inexpensive lignocellulose crop residue available in great quantities in Minnesota and generally in the corn belt of the Midwest and thus is very attractive as a biomass source for hydrothermal carbonization. (Specific results are illustrated in Activity 3, following.) The focus now is on a series of designed experiments (DOE) to determine the optimum levels of La and activating agent to maximize phosphorous sorption. This DOE is a fractional factorial with triplicate center point. The responses are phosphorous (P) sorption level and amount of lanthanum remaining in the hydrothermal carbonization (HTC) filtrate. The objective is to maximize P sorption and minimize unused La remaining in the filtrate. Isotherms for hydrochars at varying levels of Lanthanum will be utilized to determine the optimum. Achieving this will most likely require a second or follow-on DOE. Once this is established the HTC process variables of temperature and residence time will be examined in a DOE for maximum yield of hydrochar.

Activity Status as of *[July 30, 2017]***:**
An exploratory DOE has been conducted first to provide direction in selection of appropriate ranges for the independent variables. The center point of this design, which is for stoichiometric quantities of lanthanum and KOH, has been replicated four times with consistent results with respect to char yield, pH of the filtrate and phosphate removal. Before proceeding further with the DOE, material balances will be conducted for several experiments to fully understand how the active sorbent and other components are allocated between the two phases (char and filtrate) obtained in the HTC process and as a further measure of reproducibility. Additionally, experiments are being conducted to assess any differences that might exist between chars made from corn stover sources from different locations in Minnesota (Rosemont and Rochester).

Activity Status as of *[Dec.31, 2017]***:]**

Nitrates (Outcome 1)

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. Nitrate removal from water is a challenging task.
Over 25 different chars derived from diverse animal manures (cow manure; poultry manure; swine manure), agricultural residues, fermentation residues, well performing chars from P-sorption experiments and metal impregnated hydrochars were evaluated for nitrate sorption.

The best modified chars were those made from either corn stover or condensed distillers solubles (from ethanol fermentation of corn) with post addition of zinc chloride followed by thermal treatment in the absence of oxygen. These modified hydrochars had a nitrate sorption capacity comparable to a commercially available, expensive activated carbon (Filtrasorb 400) in the range of 5.6 – 8.5 mg NO_3 sorbed per gm of sorbent from a 5 ppm solution typical of agricultural waters. However, we believe

more can be done to achieve an even higher sorption capacity but it would require a concerted effort exceeding the current budget.

Comparison of Corn Stover Sources: Rochester vs. Rosemount

Corn stover herein is defined as stalks and leaves and does not include the cobs. Very early experiments were with cornstover from Rosemount, MN. Subsequently, stover sourced from Rochester, MN. was utilized for the great majority of the experiments involving stover. This was because the Rochester source could provide a sufficient quantity to ensure a single source for all the important experiments. Analysis for ash, carbon and nitrogen content revealed differences between the two sources.

- Ash is higher in Rochester stover (7.0% vs.5.3%)
- C is slightly higher for Rochester
- N is 2x for Rochester (0.82% vs. 0.42%)
- Rochester char C/N ration essentially same for char and raw stover

DOE (Outcome 2)

Based on phosphorous sorption tests and other considerations, detailed in activity 3, the decision was made to focus on post addition of lanthanum to the char after hydrothermal carbonization (HTC) of the biomass instead of in-situ addition during HTC of the biomass/lanthanum cocktail. Thus, the need for an extensive DOE for the in-situ method was eliminated by this decision. Instead a modified factorial DOE was conducted with reaction time and temperature as independent variables. The purpose of the DOE is to assist in selecting operating conditions to maximize yield and the performance of subsequent treatment by anaerobic digestion (AD) for filtrate remediation. Performance of the AD will be measured by methane production as well as COD (chemical oxygen demand) and TOC (total organic carbon). The factorial experiments have been completed and the AD experiments are in progress and will be concluded in about 30ndays.

Cost to Produce Various Hydrohars   (Outcome 3)

The cost of producing the most commonly utilized corn stover based chars in the project were estimated for;

1. Corn stover hydochar
2. Corn stover hydrochar with post thermal heat treatment
3. Corn stover hydrochar with post addition of lanthanum
4. Corn stover hydrochar with post thermal heat treatment and post addition of lanthanum.

These estimates are based on the following assumed parameters for major cost factors:
- Corn stover @ $90/short ton @ 10% moisture
- La(Cl)$_3$ hexahydrate @ $2.68/kg
- KOH @ $1.96/kg
- Capital for HTC processing plant @ $1,400,000, 10 year life, capacity of 4000t/yr of stover.

Basic Hydrochar cost is $0.22/lb.
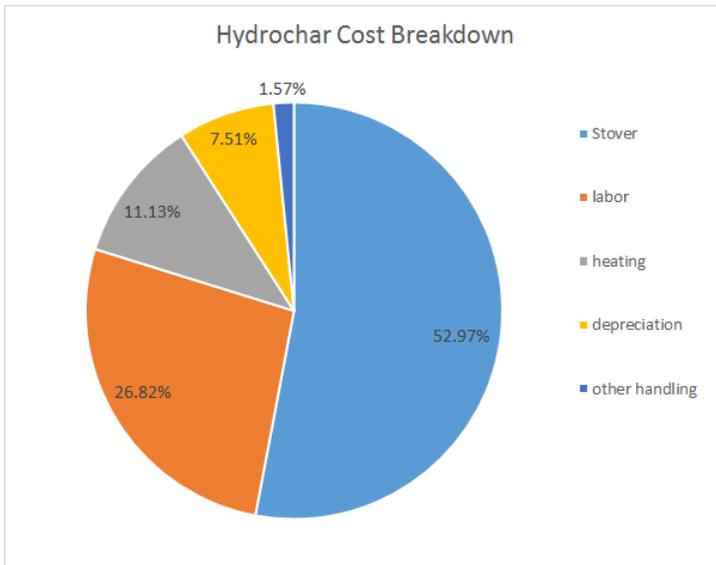
Hydrochar with post thermal heat treatment $0.53/lb
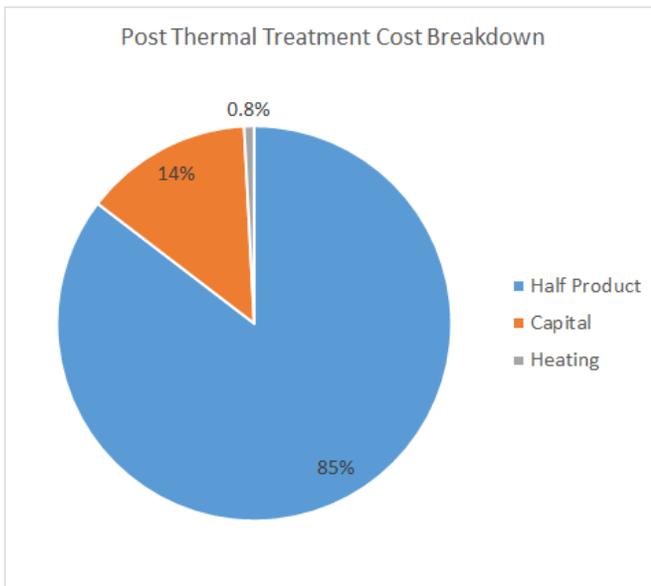
Hydrochar with post addition of lanthanum $1.74/lb

Post Addition of Lanthanum Cost Breakdown

- Cost LaCl3
- Cost KOH
- Cost Char
- Cost Depreciation
- drying
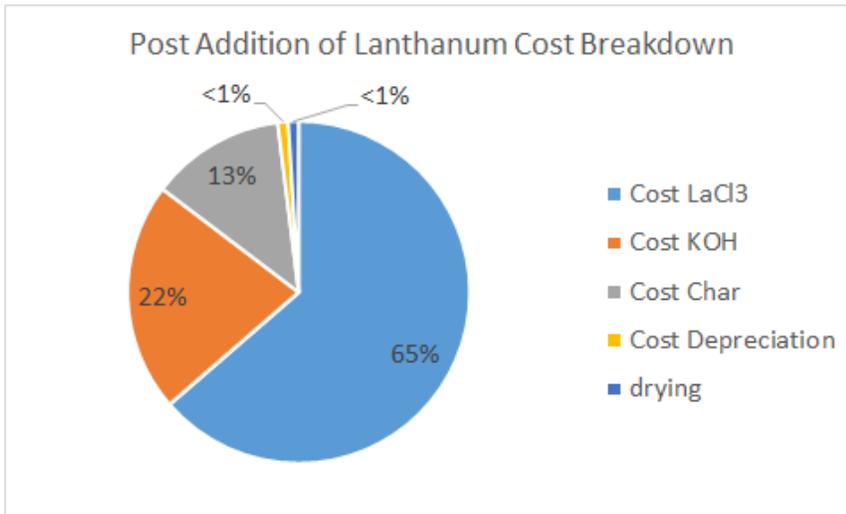
Hyrochar with post thermal heat
treatment +post addition of lanthanum $2.05/lb.
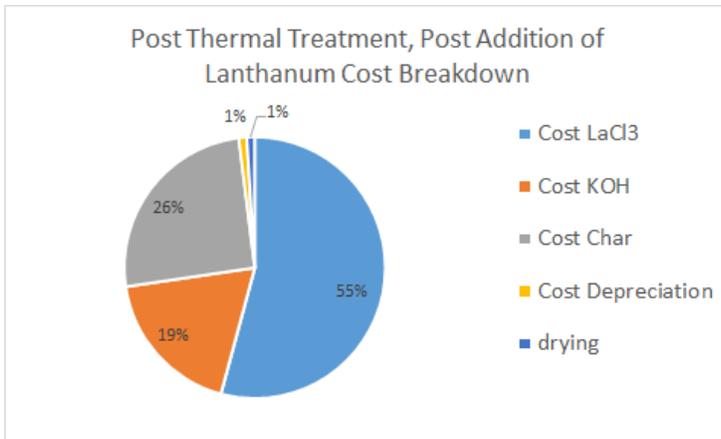
Post Thermal Treatment, Post Addition of Lanthanum Cost Breakdown

- Cost LaCl3
- Cost KOH
- Cost Char
- Cost Depreciation
- drying

Cost summary by product

Basic corn stover hydrochar	$0.22/lb
Post heat treated corn stover hydrochar	$0.53/lb
Post addition lanthanum hydrochar	$1.74/lb
Post heat treat , post add lanthanum hydrochar	$2.05/lb

Activity 1: Final Report Summary   July 31, 2018

To determine the best combination of biomass source, metals and activating agents, over 100 different hydrochars were evaluated. The biomass sources were varied and included poultry, swine and cattle and dairy manures, CDS (condensed distillers solubles from ethanol fermentation), corn stover and peat. Corn stover herein is defined as stalks and leaves and does not include the cobs. Metals that were incorporated in the hydrochars included zinc, magnesium, iron and lanthanum. Several of the produced hydrochars were post-thermally treated to modify surface chemistry.

Phosphorus removal capacity of the test hydrochars was evaluated utilizing a test solution that is typical of agricultural runoff waters (typically 2 ppm). These tests showed that the zinc and magnesium constructs sorbed 1.0 mg/kg char and 0.340mg/kg respectively at equilibrium with a 2 ppm phosphorus challenge solution. The starting hydrochar with no metal addition had no detectable sorptive capacity for phosphorous from a 2ppm solution.

Based on numerous phosphorus sorption experiments the most promising constructs were metal oxide hydrochars constructed from corn stover with Lanthanum(La) as the active metal and either potassium hydroxide (KOH) or sodium hydroxide (NaOH) as activating agent

These resulted in the highest phosphorous equilibrium sorption, in the range of 15-30 mg/gram of hydrochar, from phosphorus solutions typical of agricultural runoff waters (2-2.5ppm).

 Lanthanum is sometimes considered the first element of the 6th-period transition metals and is traditionally counted as a rare earth element. Lanthanum has no biological role in humans but is essential to some bacteria. It is not particularly toxic to humans.

Corn stover is an inexpensive lignocellulose crop residue available in great quantities in Minnesota and generally in the corn belt of the Midwest and thus is very attractive as a biomass source for hydrothermal carbonization. For these reasons, as well as ready availability, it was the biomass of choice for this project.

Important results of phosphorus sorption tests are presented in detail in Activity 3.

Preferred Method of Lanthanum addition

 Consideration was given to determine the best mode for attaching lanthanum to the hydrochar. **In-situ** addition consists of adding the lanthanum and activating agent (base) to the HTC reactor along with the biomass plus water and subjecting the combined contents to HTC processing. With this method, the lanthanum construct tends to be uniformly distributed throughout the hydrochar particles. However, there is always some residual lanthanum remaining in the residual liquid phase (filtrate). This is a concern from an economic standpoint and more importantly also presents engineering problems with recovery and /or recycle of the residual lanthanum. An alternative is to add the lanthanum and activating base to the hydrochar **in a post addition** second step outside of the reactor after the hydrochar is formed through HTC processing of the biomass alone. This **post addition** offers operational, economic and environmental advantages:

- **In-situ** lanthanum addition requires an expensive glass liner inside the reactor to mitigate corrosion from the strong base (KOH) and would need to be replaced frequently.
- There would be no Lanthanum in the HTC reactor filtrate to recover or remediate which **minimizes Lanthanum cost and avoids remediation to avoid any discharge of lanthanum to the environment.**

 Therefore, the decision was made to focus on **post addition of lanthanum** to the char after hydrothermal carbonization (HTC) of the biomass **instead of in-situ addition** during HTC of the biomass/lanthanum cocktail. Thus, the need for an extensive set of **statistically designed experiments**

(DOE) for the in-situ method was eliminated by this decision. Instead a modified **factorial DOE was conducted with reaction time and temperature as independent variables**. The purpose of this DOE was to assist in selecting operating conditions to maximize yield and the performance of subsequent filtrate remediation by anaerobic digestion (AD). The filtrate must be treated by either land application as a fertilizer or reduction in COD and BOD before discharge into municipal waste treatment systems. Performance of the AD was measured by methane production as well as COD (chemical oxygen demand). The temperature (225 -250 C) and time ranges (4-6 hrs.) in the factorial design covered the full practical range for HTC of corn stover. Over this range the COD reduction was from 75-98%. It is reasonable to conclude that anaerobic digestion for the corn stover filtrate is feasible. The choice of operating parameters for the HTC reactor can be based on maximizing hydrochar yield without much concern for impact on subsequent anaerobic digestion of the filtrate.

Cost to Produce Various Hydrochars

The cost of producing the most commonly utilized corn stover based chars were estimated for;

5. Corn stover hydrochar
6. Corn stover hydrochar with post thermal heat treatment
7. Corn stover hydrochar with post addition of lanthanum
8. Corn stover hydrochar with post thermal heat treatment and post addition of lanthanum.
9.

These estimates are based on the following assumed parameters for major cost factors:

- Corn stover @ $90/short ton @ 10% moisture
- La(Cl)$_3$ hexahydrate @ $2.68/kg
- KOH @ $1.96/kg
- Capital for HTC processing plant @ $1,400,000, 10-year life, capacity of 4000t/yr of stover.

Cost summary by product

Basic corn stover hydrochar	$0.22/lb
Post heat treated corn stover hydrochar	$0.53/lb
Post addition lanthanum hydrochar	$1.74/lb
Post heat treat, post- add lanthanum hydrochar	$2.05/lb

Nitrates

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. Nitrate removal from water is a challenging task.

Over 25 different chars derived from diverse animal manures (cow manure; poultry manure; swine manure), agricultural residues, fermentation residues, well performing chars from P-sorption experiments and metal impregnated hydrochars were evaluated for nitrate sorption.

The best modified chars were those made from either corn stover(CS) or condensed distillers solubles(CDS) (from ethanol fermentation of corn) with post addition of zinc chloride followed by thermal treatment in the absence of oxygen. These modified hydrochars had a nitrate sorption capacity comparable to a commercially available, expensive activated carbon (Filtrasorb 400) in the range of 5.6 – 8.5 mg NO_3 sorbed per gm of sorbent from a 5 ppm solution typical of agricultural waters. Some selected results for nitrate sorption as mg NO_3 sorbed per gm of sorbent:

(ZTP 10-2) CDS +ZnCl2 + ptt = 10.95   ptt = post thermal treatment

(ZTP-2-39-5) CS + ZnCl2 + ptt = 5.0

(ZTP 86-1) CS + ptt   = 6.05

However, our work on nitrate removal, while very promising, was at the very early stage of development and would require a substantial effort to increase nitrate sorption of the hydrochar to levels that would be meaningful for agricultural drainage applications. A proposal to do this was submitted to LCCMR in the 2017 RFP but was not selected for funding.

Budget considerations dictated a focus on phosphorous and pesticide remediation for this project.

Conclusions

- **Lanthanum modified hydrochars have best phosphorus removal capacity**
- **Post addition of La to hydrochar is preferred method**
- **Cost of lanthanum modified chars driven by Lanthanum cost**
- **Zinc chloride modified bio-hydrochar sorbs nitrates comparably to Filtrasorb 400 activated carbon**

All activity 1 outcomes have been completed

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:	**$ 48,375**
Balance:	**$ 0**

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, 2017
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, 2018

Activity Status as of *Dec.31, 2015***:** Preliminary experiments were directed at the use of headspace gas analysis to characterize chars made from CDS for sorbed volatile components. An important question to be resolved is whether hydrochars sorb compounds present in the HTC filtrate?

The resulting GC-MS chromatograms of the filtrate and hydrochar suggest very limited sorption by the hydrochar of compounds present in the filtrate. Instead, the hydrochars possess their own unique signature that is dominated by the presence of aldehydes (e.g., pentanal, hexanal, and heptanal). These compounds are used in fragrances, lubricants, and resin production; and could be partially responsible for the hydrochar odor. The absence of these aldehydes in the filtrate is likely due to the use of flashing of steam to cool the HTC reactor contents after completion of the reaction. Further research is being conducted in this area.

Activity Status as of *[July 30, 2016]***:**
Staff was trained in the operation of the FTIR instrumentation in the UMN Surface Characterization Laboratory (CharFac) for surface chemistry characterization. The hydrochars produced in Activity 1 are currently being analyzed. In addition samples have been sent to an outside laboratory for proximate and ultimate analyses. These results should be available for the next reporting period.

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

Greenhouse Gas (GHG) impact incubations have been initiated for ten (10) hydrochar samples of various types. Biolog plates (a device to measure substrate uptake of known carbon sources such as glucose, sucrose, fructose, carbohydrates, etc.) have been acquired to assess the microbial impact of these hydrochars. Extractions will be performed after the GHG impact in the coming months. Proximate and ultimate analysis results are still pending.

Activity Status as of *[July 30, 2017]***:**
Results from green- house gas incubations have provided insight into more complex interactions occurring between HTC production variables (temperature, reaction time) and additives to enhance phosphate sorption (Lanthanum, KOH). More detailed experiments to elucidate the important factors are being conducted.

Reproducibility and Material Balance of HTC production

Producing hydrochars from biomass involves several steps that include weighing of biomass, water addition, reactor temperature control, reaction time, product recovery from the Paar reactor,(char and filtrate), washing of char to reach consistent pH and electrical conductivity (EC). These steps are all subject to experimental error or variability. It is important to have consistency in the physical and chemical properties of the char and filtrate produced in hydrothermal carbonization experiments and to be able to reproduce essentially the same char and filtrate from run to run. Many experiments on chars and filtrate often require more material than can be produced in a single run due to the physical size of the Paar reactors that are feasible for laboratory scale work. Thus, reproducibility from run to run is essential to have confidence that results observed in subsequent experiments are due to intentional changes in experimental parameters and not a manifestation of experimental error.

To evaluate the reproducibility of the hydrothermal carbonization (HTC) process of Rochester corn stover three replicates at two different temperatures were conducted. Each run consisted of a heating step to set temperature of 225 °C or 250 °C and reaction time of 4 hours. The char was separated from the filtrate and washed a sufficient number of times (5-6) in DI water to reach a constant EC. Responses were yield of char and filtrate, and C and N analysis of both char and filtrate. These results were then subjected to statistical analysis of variance to determine;

1. Variability within the group at the two different temperatures and
2. Whether the two groups were significantly different

Subjecting the data to a statistical analysis of variance (Tukey HSD test and Kruskal-Wallis rank sum test) clearly showed that the results within each group were reproducible and that the observed differences between groups were real and reproducible as well. For these particular experiments the char yield at 225 ^{0}C was 44.2 % and was 37.8% at 250 ^{0}C.

In addition to reproducibility between runs it is also important to be able to account for all the material before and after a run in the form of a **material balance**. The distribution of carbon (C) and nitrogen (N) between the char and filtrate can be used for subsequent analysis and scientific inquiry. In a Parr reactor there are 4 product streams to consider for a material balance; 1. Char, 2. Filtrate or residual liquid, 3. Liquid retained by char after separation from residual liquid, and 4. Gases produced during the reaction. The first three streams are readily measurable. However, the gas stream is problematic to determine accurately from both a quantity and composition standpoint. In this case the quantity of gas was obtained by weighing the reactor before and after completion of the run. The gas stream can contain water, carbon dioxide, carbon monoxide, methane, and various other gases. If one assumes that the gas is all carbon dioxide then closure is achieved. For the char made at 225^0 C the results are illustrated in the pie chart below. Results are similar for the material made at 250^0 C.
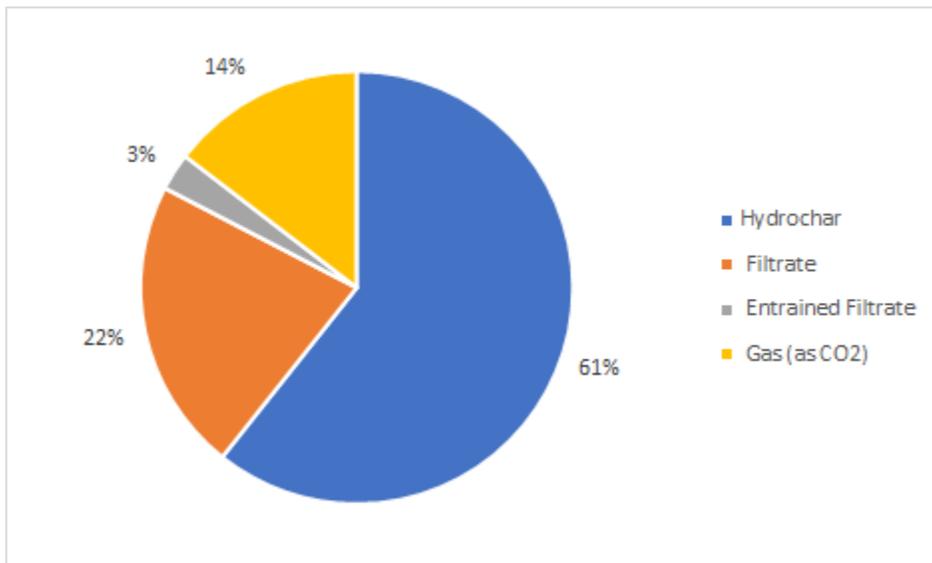
Material balance for reaction at 225^0 C

Final Report Summary: July 30, 2018

Activity 2 Final Report Summary, July 30, 20018

Greenhouse Gas Impacts: Outcome2

The impact of the various hydrochars on the soil microbial community were assessed with greenhouse gas production incubations. For these assessments, 5 g of an agricultural field soil (taken from Rosemount, MN) were placed into a 120 mL serum bottle. Following this, the various treatments (approximately 1% by weight addition) of the hydrochar were also added to the respective treatments. Deionized water was added to bring the incubation up to field capacity and then sealed with a butyl rubber septa and aluminum crimp. These incubations were run at a minimum in triplicate. The various treatment results are summarized in Table 1.

Table 1 – Results of Greenhouse Gas Incubations

TREATMENT	CO$_2$ (μg C g^{-1} d^{-1})		CH$_4$ (ng C g^{-1} d^{-1})		N$_2$O (ng N g^{-1} d^{-1})		O$_2$ (μg O g^{-1} d^{-1})		N$_2$ (μg N g^{-1} d^{-1})	
CONTROL	15.87 (1.2)	a	0.12 (0.01)	a	8.22 (0.6)	a	-35.5 (4.5)	b	46.04 (10.9)	a
RAW CS	**82.7 (21.76)**	b	0.13 (0.06)	a	7.34 (3.45)	a	**-251.99 (68.24)**	a	**10.21 (15.81)**	b
HTC CHAR	17.25 (0.54)	a	0.09 (0.02)	a	**1.42 (0.85)**	b	-43.67 (5.95)	b	18.2 (7.93)	ab
PTT CS	15.32 (0.42)	a	0.02 (0.07)	a	**2.98 (1.16)**	b	-42.54 (5.25)	b	10.62 (24.78)	ab
PTT CS-W	15.27 (0.67)	a	0.1 (0.04)	a	**1.25 (0.95)**	b	-38.97 (3.65)	b	23.5 (11.99)	ab
PTT HTC	15.4 (0.23)	a	0.05 (0.04)	a	**0.35 (0.15)**	b	-40.18 (6.74)	b	23.33 (20.19)	ab

Discussion

N_2O Production:

There was a significant decrease observed in N_2O production as a consequence of the HTC and PTT amendments ($P<.05$; Figure 1). There were no detectable differences between the treatments, but as a class of materials they all reduced N_2O production in this laboratory incubation. This is similar to results commonly observed for carbonized amendments for N_2O (Sánchez-García et al., 2014).
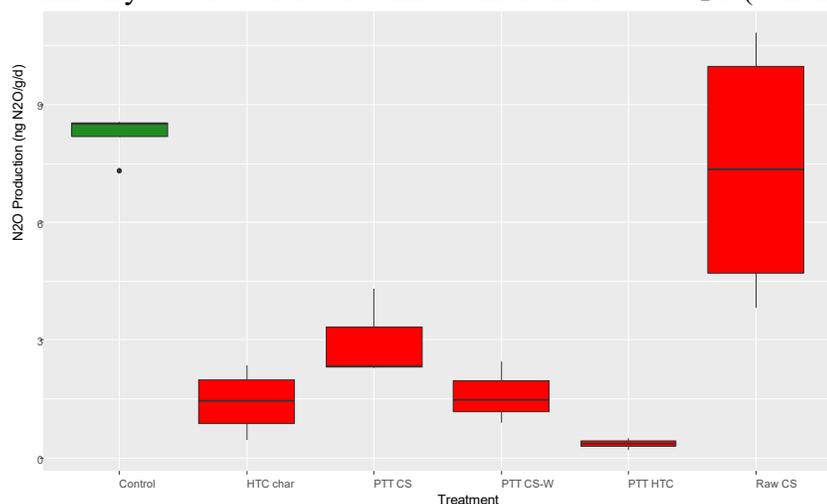
Figure 1. Production of N_2O (ng N g^{-1} d^{-1}) from the laboratory incubations

CO_2 Production:

There was a significant increase in CO_2 production resulting from the corn stover addition ($P<0.05$; Figure B). Despite the significant reductions observed for the N_2O production (Fig. b), there were no statistically significant differences observed for the hydrochar and PTT products for CO_2 production (shown in the inset in Fig. 2). This is an interesting observation given the drastic reduction observed for N_2O is assumed to arrive from a microbial impact on the amended soil system (e.g, Sánchez-García et al., 2014).
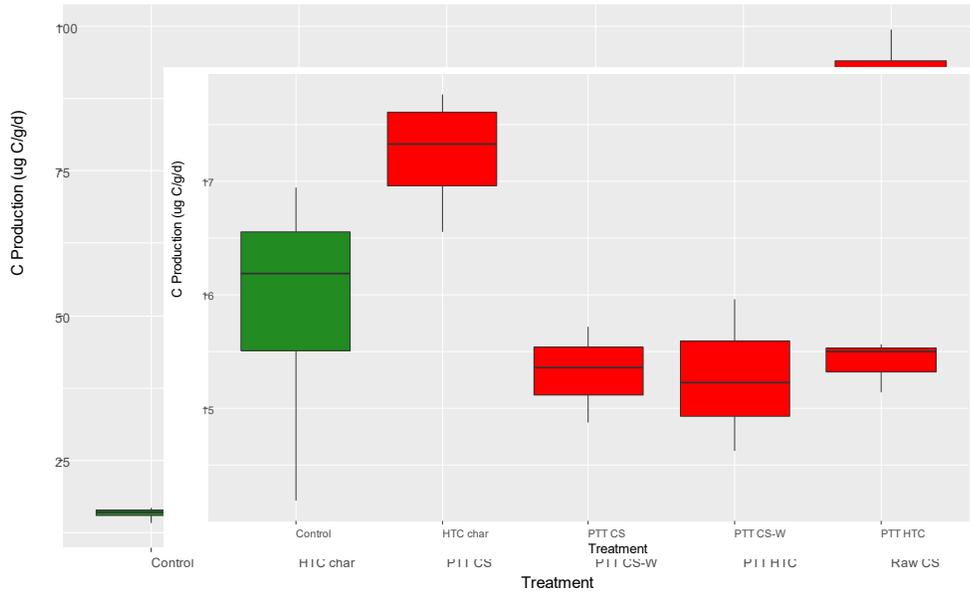
Figure 2. Observed alterations in the CO$_2$ production rates as a function of the treatments

CH$_4$ Production:

There were no statistically significant differences observed for the hydrochar and PTT products on CH$_4$ production (Fig. D).
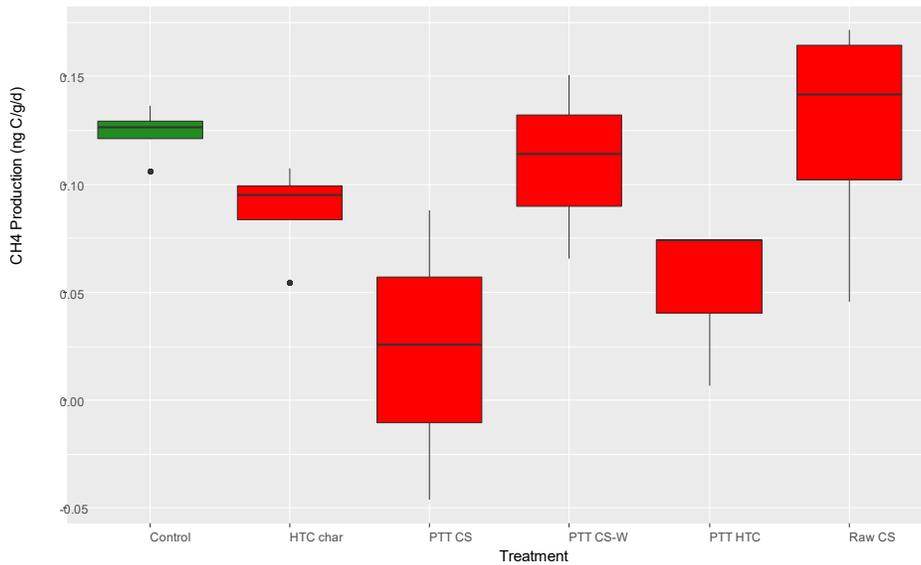
Figure 3. CH$_4$ Production

O$_2$ Consumption:

There was a statistical increase in O$_2$ consumption because of the raw corn stover addition (P<0.05; Fig. 4). This is also demonstrative that the microbial mineralization is stimulated in the raw corn stover additions. The fact that the O$_2$ consumption was higher suggests a stimulation in the microbial metabolism rates, which is linked to the higher CO$_2$ production (Figure 2).
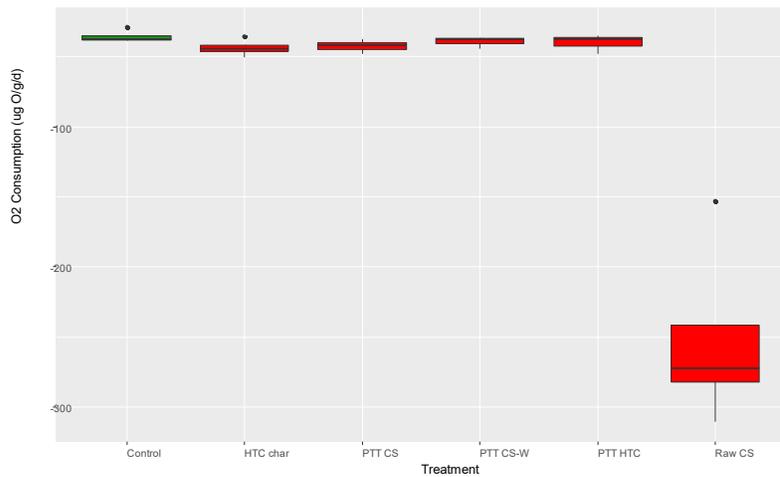
Figure 4. Oxygen Consumption

N$_2$ Production:

Contrary to the statistically significant differences in the N$_2$O production rates, there were no statistically significant differences observed in the rates of the N$_2$ gas production as a function of the amendments (P>0.05; Figure 5).
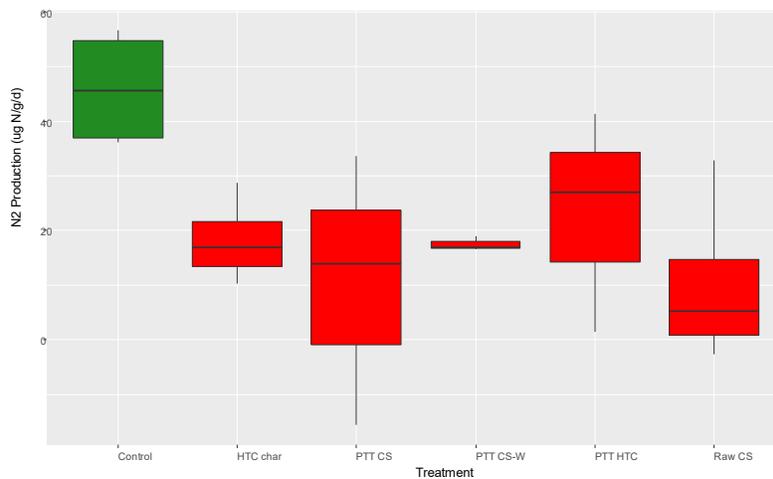
Figure 5. Nitrogen production rates as a function of the treatment in the laboratory incubations.

Conclusions and Significance for greenhouse gas effects:
There was a statistically significant suppression in the production of N$_2$O following hydrochar additions. However, the reduction in CO$_2$ production was not statistically significant. The only observable difference in oxygen consumption was for the raw corn stover. These factors would suggest that the mitigation of N$_2$O production is stronger than the hydrochar suppression on the total microbial population

Reference:

Sánchez-García, M., Roig, A., Sánchez-Monedero, M.A., Cayuela, M.L., 2014. Biochar increases soil N2O emissions produced by nitrification-mediated pathways. Frontiers in Environmental Science 2, 25. https://doi.org/10.3389/fenvs.2014.00025

Activity 2 Final Report. Outcome 1

Reproducibility
Frequently, experiments on hydrochars and filtrate require more material than can be produced in a single run due to the physical size of the Paar reactors that are feasible for laboratory scale work. Thus, reproducibility in the physical and chemical properties of the char and filtrate, from run to run is essential to have confidence that results observed in subsequent experiments are due to intentional changes in experimental parameters and not a manifestation of experimental error.
To evaluate the reproducibility of the hydrothermal carbonization (HTC) process for corn stover three replicate runs at two different temperatures were conducted. Each run consisted of a heating step to set temperature of 225 °C or 250 °C and reaction time of 4 hours. The char was separated from the filtrate and washed a sufficient number of times (5-6) in DI water to reach a constant EC (electrical conductivity). Responses were yield of char and filtrate, and C and N analysis of both char and filtrate. These results were then subjected to statistical analysis of variance to determine;

3. Variability within the group at the two different temperatures and
4. Whether the two groups were significantly different

Subjecting the data to a statistical analysis of variance (Tukey HSD test and Kruskal-Wallis rank sum test) clearly showed that the results within each group were reproducible and that the observed differences between groups were real and reproducible as well. For these particular experiments the char yield at 225 ^{0}C was 44.2 % and 37.8% at 250 ^{0}C.

Material Balance
It is important to be able to account for all the material before and after a run in the form of a **material balance**. The distribution of **carbon (C) and nitrogen (N)** between the char and filtrate can be used for subsequent analysis and scientific inquiry. In a Parr reactor there are 4 product streams to consider for a material balance; 1. Char, 2. Filtrate or residual liquid, 3. Liquid retained by char after separation from residual liquid, and 4. Gases produced during the reaction. The first three streams are readily measurable. However, the gas stream is problematic to measure accurately from both a quantity and composition standpoint. In this case the quantity of gas was obtained by weighing the reactor before and after completion of the run. The gas stream can contain water, carbon dioxide, carbon monoxide, methane, and various other gases. If one assumes that the gas is all carbon dioxide then closure is achieved. For the char made at 225^0 C the results are illustrated in the pie chart below. Results are similar for the material made at 250^0 C.
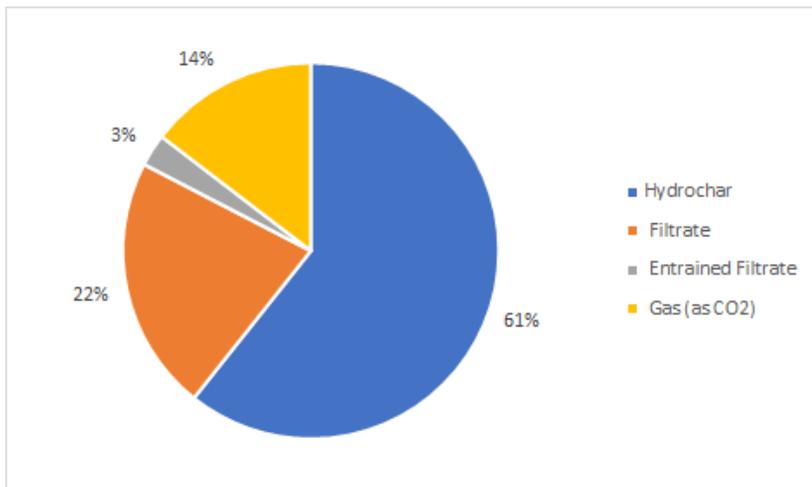
Material balance for reaction at 225⁰ C

C/N Analysis

The total amount of C and N present in a sample was determined on an elemental analyzer (VarioMax Cube;). A small sample (approximately 0.75 g) was placed into a stainless-steel crucible and then tested on the instrument. The average of triplicate samples was computed and the standard deviation was used as an assessment of variability in the solid product (Table 2). Overall, there was good homogeneity observed in the HTC and PTT samples. The maximum variability was seen in the composite sample (highlighted).

Table 2. C and N analysis of various hydrochars

	%C	STDEV	%N	STDEV	
ZTP 109 114 116	66.84	2.39	1.349	0.05	
ZTP122	69.47	1.28	1.277	0.03	
ZTP123	65.12	0.70	1.096	0.02	
ZTP124	67.98	0.04	1.215	0.01	
ZTP140	45.68	0.06	0.770	0.02	
ZTP2-108	71.77	0.52	0.641	0.02	
ZTP2-111	64.42	1.13	0.534	0.03	
ZTP2-126-1	69.69	0.06	1.375	0.003	
ZTP2-126-2	60.65	NA	1.231	NA	
ZTP2-126-3	64.31	2.10	1.259	0.039	
ZTP2-126-4	65.58	4.37	1.28	0.039	
ZTP2-126-5	68.32	4.67	1.325	0.09	
ZTP2-128-3	73.46	0.08	0.825	0.015	
ZTP2-88	68.36	0.12	1.267	0.0115	
ZTP82	61.75	0.24	0.977	0.019	

The average C content of all the chars tested was 67% with a range of 61.75 -73.5%. The raw corn stover had a C value of 45.7% so the HTC process removes sufficient hydrogen and oxygen to concentrate the C rom 45.7 to 67% on average.

Surface and Microstructure Characterization of Chars

Pore volume estimates

Pore volume was estimated by allowing the submerged sample to sit in a vial filled with DI water and then placed into a desiccator in which a vacuum of -22.5" Hg (house vacuum supply) for 24 hours (Figure 6).

Connected to vacuum line

Sample submerged in DI water

(A)   (B)
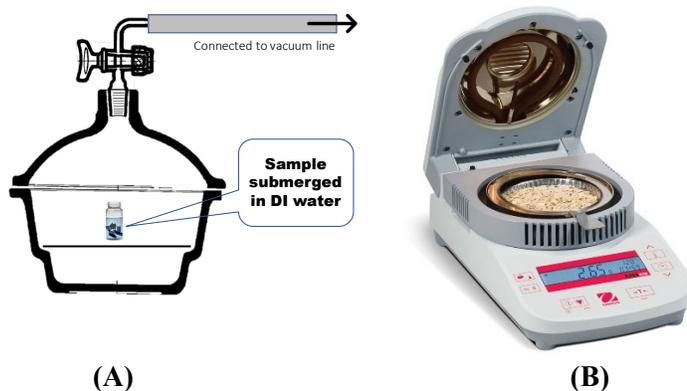
Figure 6. (A) Desiccator with sample submerged in DI water and vacuum pulled for 24 hours. (B) Sample moisture determined on a moisture balance (*Ohaus MB23*).

After this equilibration time, the samples were removed from the desiccator [filtering on very coarse filter paper (>20 µm)] and then placed on a soil moisture balance to determine the gravimetric water content in this drained saturated state (Fig. 2B). The conditions for drying on the balance were 115 °C and held until there was <1 mg change in 90 seconds. In other words, a rate of water loss $<= 1.11 \times 10^{-5}$ g s^{-1}.

The data from the balance was captured via the serial port and recorded using a customized computer program (C#), which logged the mass and temperature of the balance every 3 seconds for later analysis in Excel®. This balance data was used initially here for the pore volume (total gravimetric moisture at saturation) and then later for the drying curve analyses (Section C.3).

To estimate the pore volume (cm^3 g^{-1}), the gravimetric water content (g H$_2$O g^{-1} wet solids) was converted to a dry basis (g water g^{-1} dried solids), and then the density of water was assumed to be 1.0 g cm^{-3} to permit the calculation of the total pore volume that was filled with water. These results are shown in Table 2.

Table 2. Drying rates, times and pore volumes for isothermal drying (115 ºC)

Sample ID	PTT	HTC		Drying Time (sec)	k $(g_{water}\ g^{-1}_{material}\ S^{-1})$	Pore Volume $(cm^3/100\ g_{dry})$
CS			Raw	15:15	0.0995	11.79
ZTP2-121	✘		PTT of CS	17:45	0.148	7.62
ZTP2-121W	✘		PTT of CS (washed)	18:18	0.099	8.27
ZTP2-88		✘	High Temp HTC	9:36	0.199	4.07
ZTP2-141	✘	✘	PTT high Temp HTC	12:45	0.124	2.58
ZTP2-114	✘	✘	PTT high T HTC	7:18	0.177	3.92
ZTP2-128	✘	✘	PTT low temp HTC	15:15	0.125	5.39

Results:

Surprisingly, the total pore volume decreased from the raw feedstock because of the thermal treatments, with the highest temperature product (high temp HTC and PTT; ZTP-2-114/141) was observed to possess the smallest pore volume determined by the method used here (25% of the original volume).

This contrasts with the HTC literature, in which researchers have typically observed higher pore volumes measured with increasing BET N_2 surface areas (i.e., Mumme et al., 2011; Fernandez et al., 2015). Typically for hydrochars, individuals use the nitrogen BET and estimate the volume of micro-pores by the Dubinin–Radushkevich equation (Stoeckli, 1977) and the volume of meso-pores was estimated as the difference between total pore volume and micro-pore volume. This has justified the conclusion that HTC increases the surface area and total pore volume following HTC. However, our data suggests that this may not be the case for water at room temperature. There are several potential theoretical explanations for these observations. One possibility is that since N_2 BET surface area assessments are made at 77ºK but in practical applications involving sorption from water at essentially ambient temperature small intermolecular forces could ultimately prevent water molecules from entering the internal pore structure of the char. This would imply a "theoretical BET" value at near absolute zero conditions and a more realistic value seen at ambient conditions. Further research is extremely vital to further assess the actual behavior of these materials at conditions closer to those of the ambient environment.

Comparing HTC-high temperature treatment to raw feedstock:
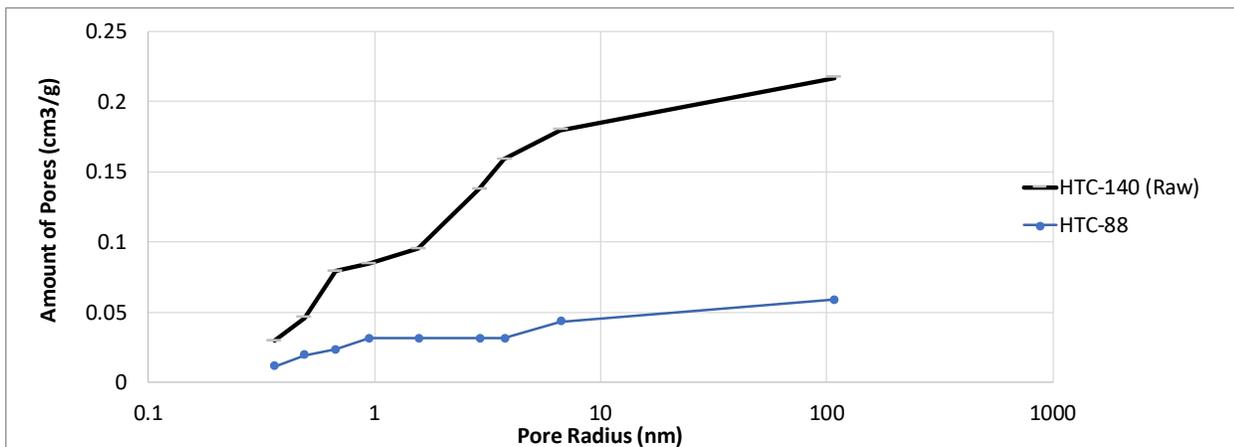
Figure 7. HTC treatment (HTC88)vs. Raw corn stover (HTC 140)

The difference in pore size distribution following the various treatments is striking. For the HTC treated materials, there is a 73% reduction in the volume of pores. A majority of the reduction occurs in the larger size fraction (radii from 1 to 100 nm) (Fig. 7). There is also loss in the small pore volume (<1 nm) of 60% compared to the original biomass.

On the other hand, thermal treatment (PTT) of the corn stover only reduces the pore volume by 30-40%. When compared to HTC, the PTT treatment preferentially lost pore volume in the larger pore fraction (>1 nm), and possessed similar pore volumes in the smaller fraction (<1 nm) (Fig. 8). However, we do not know if this is preservation of the original small pores or additional formation of small pores at the expenses of the larger pores. Overall, there is a favored loss of pore volume in the larger pores (>1 nm) with thermal treatment (Fig. 8). However, no gain in porosity was observed for water vapor at ambient conditions.
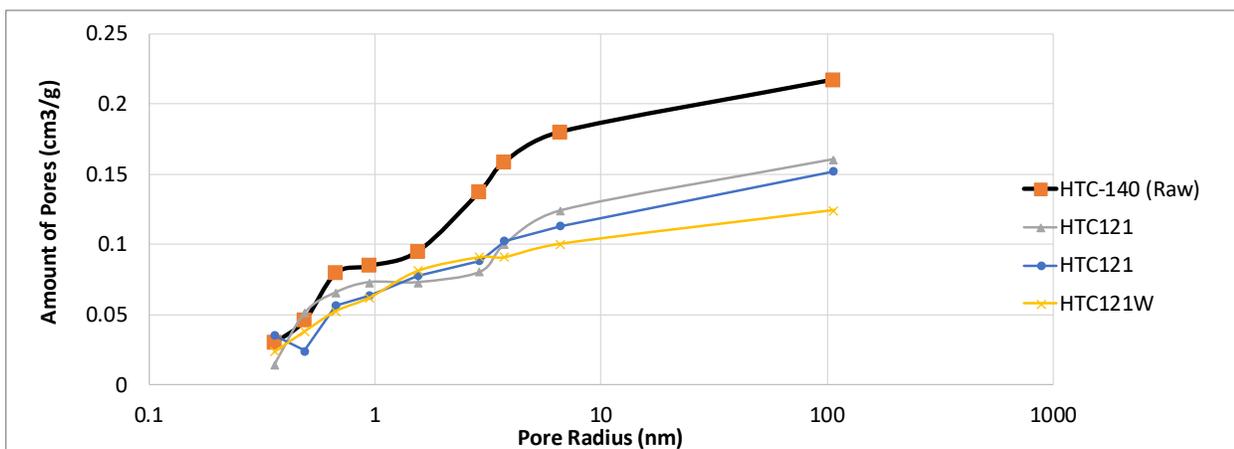
Figure 8. PTT treated (HTC 121,121W) vs. Raw corn stover (HTC 140)

In summary, HTC destroys a significant amount of the original biomass porosity, while PTT preserves more of the structural porosity in the char product. Therefore, HTC treatment results in a more complete destruction of the native biomass material (as seen in the reduction across all pore sizes). However, due to the structural disintegration of the material, the total surface area and porosity are both negatively impacted

Comparison of HTC plus PTT treated products:
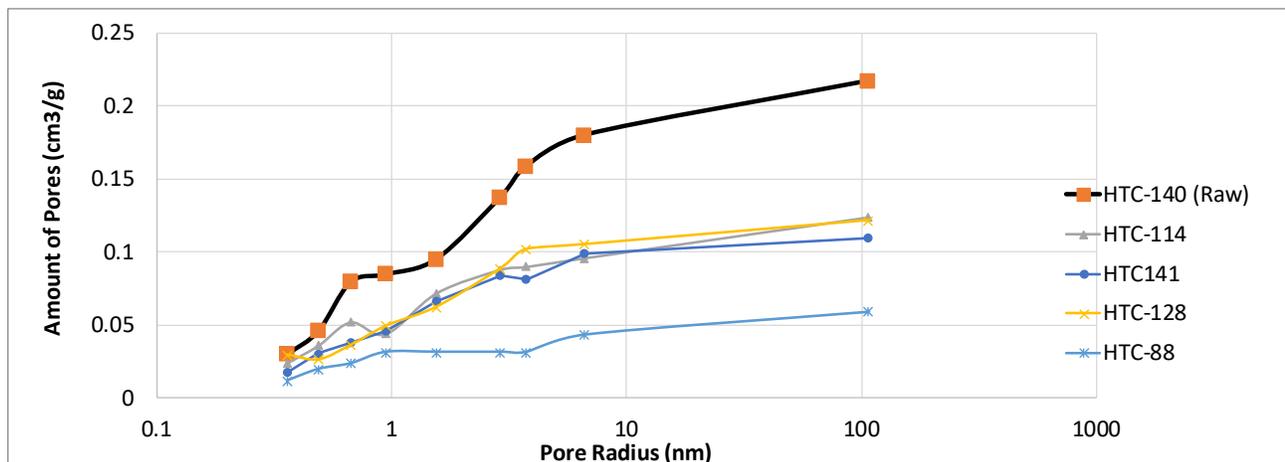
Figure 9. Comparison of the difference in pore size distribution for the raw corn stover (HTC-140), HTC treated (HTC-88), and the PTT of the HTC products (HTC-114, 141, and 128).

There is an increase of nearly 2-times the pore volume following PTT treatment of the HTC product (0.05 to 0.1 cm^3/g) (Fig. 9), but this increase is still below the original feedstock value (0.118 cm^3/g). This increase in pore volume could be due to the removal of sorbed organic chemicals on the surface of the char following HTC processing. The other possible scenario is the formation of new structures and pores during the PTT process. We attempted to examine the products with SEM to identify structural alterations.

It is interesting to note, that there is some suggestion supporting the formation of new pores in our data. The HTC and HTC+PTT treatments are slightly higher in the cumulative pore distribution plot at 1-3 nm (blue arrows; Fig. 10). These differences would be consistent with the formation of new pores in this size range. Overall, it is important to remember that despite this increase in distribution of pores, there is still a significant reduction in total pore volumes.
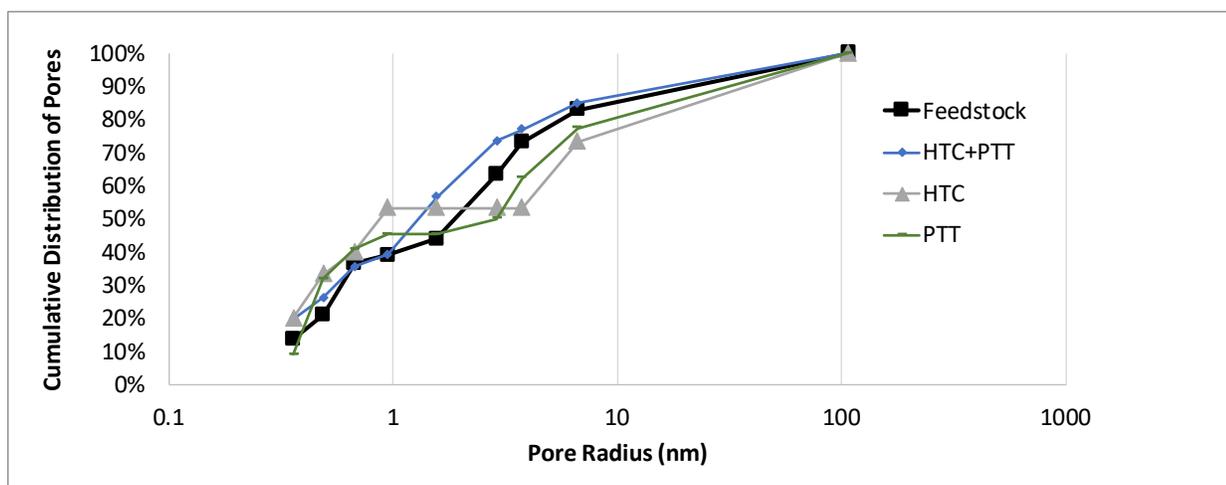
Figure 10. Comparison of the cumulative distribution of the pore size volumes across the various treatments.

Conclusions and Significance:

- **HTC increases the carbon content of corn stover from 46% to about 67% through the elimination of hydrogen and oxygen.**
- **Surface area and pore volume measurements by N_2 BET measurement may not be relevant for sorption from water at ambient conditions.**
- **PTT treatment of HTC chars significantly increases pore volume of the starting hydrochar. This has practical significance when applied to hydrochars made from high water content (>90%) slurries such as manures.**

References:

Fernandez, M.E., Ledesma, B., Román, S., Bonelli, P.R. and Cukierman, A.L., 2015. Development and characterization of activated hydrochars from orange peels as potential adsorbents for emerging organic contaminants. Bioresource technology, 183, pp.221-228.

Mumme, J., Eckervogt, L., Pielert, J., Diakité, M., Rupp, F. and Kern, J., 2011. Hydrothermal carbonization of anaerobically digested maize silage. Bioresource technology, 102(19), pp.9255-

Stoeckli, H.F., 1977. A generalization of the Dubinin—Radushkevich equation for the filling of heterogeneous micropore systems. *Journal of Colloid and Interface Science*, 59(1):184-185. 9260.

ACTIVITY 3: <u>Real-time monitoring of P/NO$_3$ sorption. Activity starts in Jan.</u> **2017**

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.

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, 2018
2. Determine change in indices (P saturation and S_{max}) as function of hydrochar application rates for 3 Minnesota soil types.	June 30, 2018

No work performed for period July1,2015 –December 31,2015.

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

FTIR analysis is currently being utilized to study phosphorous sorption by metal containing hydrochars produced in Activity 1. Nitrate will be examining in upcoming periods.

Initial results confirm that Lanthanum (La) addition prior to the HTC process (in-situ) does significantly increase phosphorous sorption capacity compared to metals such as zinc. Conversely, Lanthanum addition after the HTC process (post addition) increases sorption capacity of the hydrochar to about 30% of the in-situ method..

This finding was further explored with scanning electron microscopy (SEM) that confirmed that the in-situ addition of Lanthanum during the HTC process results in a char with a uniform coating of La on the char surface. On the other hand, post addition of La to the HTC hydrochar does not yield a char with uniformly bound Lanthanum.

Current research is focused on other metal cations to determine if this effect is unique to Lanthanum or if other cations will impart an enhanced phosphorous sorption capacity to the hydrochars.

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

Various metal cations (lanthanum, magnesium, iron) have been incorporated into hydrochars made from corn stover utilizing either potassium hydroxide (KOH) or sodium hydroxide (NaOH) as activating agents. Lanthanum oxide hydrochars are superior in phosphorous sorption to all other metal oxide constructs. First results with the lanthanum constructs show phosphorous sorption in the range of 15-30mg/gram of hydrochar from 2.5ppm solution while the other metals show near zero sorption.

The activating agent selection between KOH and NaOH results in Lanthanum oxide chars with good sorption properties but somewhat different isotherms as illustrated below.

Adsorption Isotherm - ZTP78 vs. ZTP123
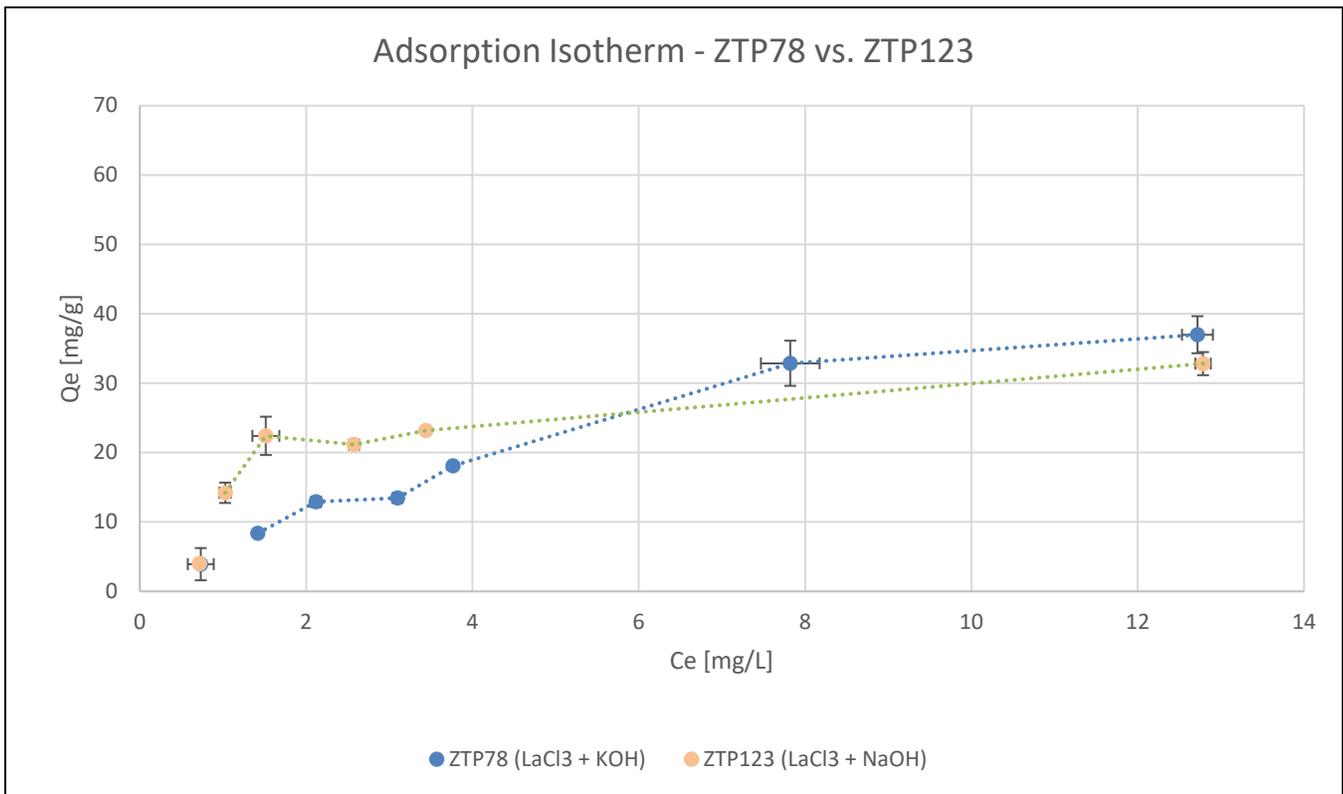
The NaOH activator imparts a higher sorption capacity in the low end of phosphorous concentration and has a similar capacity at the high end of phosphorous concentration. However, kinetic rate is not the only issue to consider as the quantity of lanthanum needed to achieve the desired sorption kinetics will impact the economics. This is yet to be determined.

Related metals other than Lanthanum are being evaluated. These may provide some advantageous properties that could be useful in the production of the activated hydrochar and in the detection of captured phosphorous by the hydrochar.

Activity Status as of *[July 30,2017]*:
Experiments have been focused on determining the best mode for attaching lanthanum to the hydrochar. **In-situ** addition consists of adding the lanthanum and activating agent (base) to the HTC reactor along with the biomass plus water and subjecting the combined contents to HTC processing. With this method, the lanthanum construct tends to be uniformly distributed throughout the hydrochar particles. However, there is always some residual lanthanum remaining in the residual liquid phase (filtrate). This is a concern from an economic standpoint and more importantly also presents engineering problems with recovery and /or recycle of the residual lanthanum. An alternative is to add the lanthanum and activating base to the hydrochar outside of the reactor after the hydrochar is formed through HTC processing of the biomass alone. This **post addition** offers several potential advantages:

- In-situ lanthanum addition requires an expensive glass liner inside the reactor to mitigate corrosion from the strong base (KOH) and would need to be replaced frequently.

- There would be no Lanthanum in the HTC reactor filtrate to recover or remediate which minimizes Lanthanum cost and avoids remediation to avoid any discharge of lanthanum to the environment.

- It is possible that post addition yields an amorphous lanthanum hydroxide coating because of the lower temperature for post addition whereas in-situ addition, conducted at a much higher temperature, results in a lanthanum hydroxide crystalline structure on the hydrochar. An

38

amorphous structure with irregularities and "bumps" could present a higher surface area for phosphorous removal as compared to the crystalline structure and thus positively influence the rate of phosphorous sorption. (R1) This is, however, not expected to alter the phosphorous binding capacity since that is dependent on lanthanum concentration present on the char.

Kinetic curves for post vs. in-situ lanthanum addition are shown in Figure 1 below.
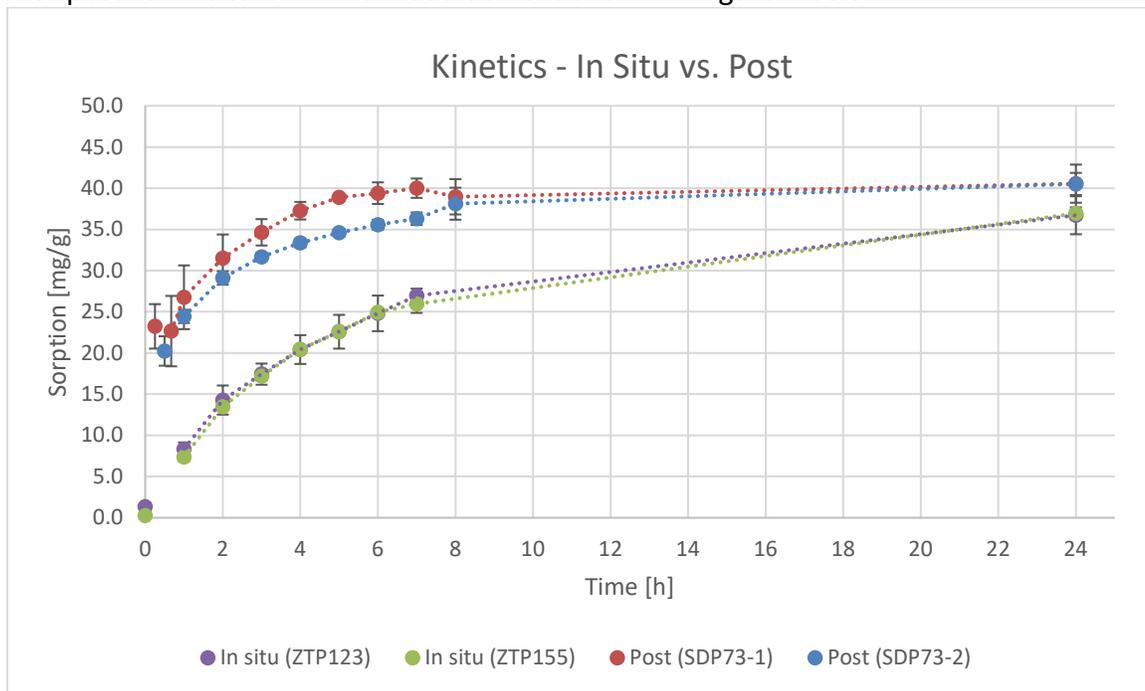
Figure 1: Kinetic curves for hydrochar with in situ addition (ZTP123 and ZTP155), hydrochar with post addition (SDP73-2) and biochar with post addition (SDP73-1). The two upper curves are for post addition and the two lower curves are for in-situ addition.

Post addition of lanthanum produces faster binding of phosphorous (Fig. 1). However, phosphorous binding capacity is essentially the same for post and in-situ addition of lanthanum since the lanthanum content of the two alternatives is the same. Within the first 30 min over 40% of the available phosphorus was removed from a solution of 25ppm phosphorous. For this treatment hydrochar (SDP73-2) and biochar (SDP73-1) were treated with $La(NO_3)_3$ and KOH. Available lanthanum is deposited directly onto the surface of the hydrochar. In situ hydrochars were produced at 225 °C and differed only in caustic bases used in the HTC process: i) ZTP123 with NaOH; ii) and ZTP155 with KOH.

R1 J. Xie, Z.Wang, S. Lu, D. Wu, Z. Zhang, H. Kong, "Removal and Recovery of Phosphate from Water by Lanthanum Hydroxide Material", Che. Eng. Journal, 254, 2014, (pp. 163-70)

Activity Status as of *[Dec 31, 2017]***:**

Lanthanum Post Addition Progress

Extensive testing has been conducted to determine the best method of lanthanum modification for hydrochars with respect to phosphorus sorption capacity and economic considerations. Two methods which have been investigated are:

1. lanthanum addition after hydrothermal carbonization treatment of biomass (post addition) and
2. lanthanum modification of the hydrochar during hydrothermal processing (in situ).

In the July 2017 update, there were 3 advantages identified for post addition of lanthanum versus in situ. They were that:

- a glass liner is not required for post addition, that
- there is no lanthanum in the filtrate product from hydrothermal carbonization treatment when post addition is utilized, and that
- the post addition hydrochar product had more favorable kinetics for phosphorus sorption from aqueous solutions.

Throughout our additional experiments since the last report, 21 combinations of biomass source, hydrochar source, and other support materials as well as varying chemical treatments have been tested. Phosphate sorption from a 50ppm phosphorous test solution showed a range of 20.8 – 45.1 mg phosphorous/gm char depending primarily on the whether or not the matrix was thermally treated prior to lanthanum addition as well as the chemistry of the lanthanum cocktail utilized. Sorption isotherms are needed to determine if this observed difference between thermally treated and untreated supports reflects true capacity differences or simply different kinetics ultimately resulting in the same equilibrium capacities.

Supports other than biomass and biomass chars were evaluated as well. Sand did not perform well and zeolite was in the range of the biomass supports. However, zeolite would be considerably more expensive than a biomass support.

Work is currently underway to determine the optimal ratio of hydrochar to lanthanum during the addition process in order to maximize lanthanum loading and phosphorus sorption efficacy. Sorption isotherms will also be determined.

Final Report Summary: July 30, 2018

Activity 3: Final Report Summary July 31, 2018

As discussed in the Activity 1 summary, that based on numerous phosphorus sorption experiments the most promising constructs were metal oxide hydrochars made from corn stover with Lanthanum(La) as the active metal added in-situ and with either potassium hydroxide (KOH) or sodium hydroxide (NaOH) as the activating agent. These constructs resulted in the highest phosphorous equilibrium sorption, in the range of 15-30 mg/gram of hydrochar, from phosphorus solutions typical of agricultural runoff waters (2-2.5ppm).

The activating agent selection between KOH and NaOH results in Lanthanum oxide chars with good sorption properties but somewhat different isotherms as illustrated below.
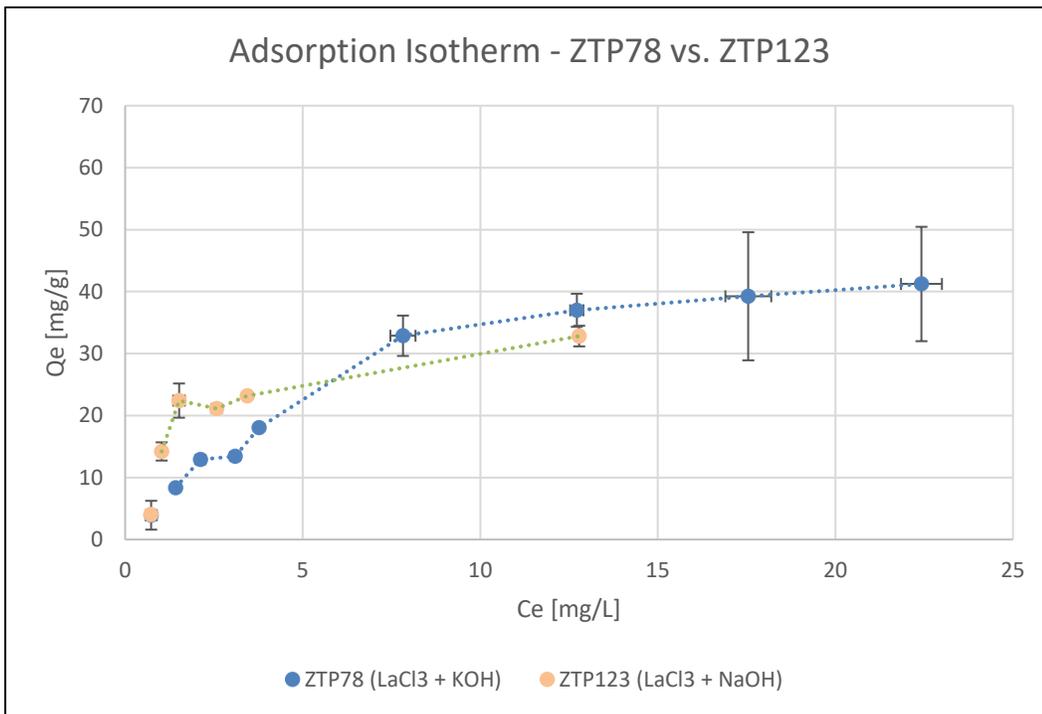
Adsorption isotherms for in-situ La-chars (ZTP78 and ZTP123) with KOH and NaOH activator respectively

The NaOH activator imparts a higher sorption capacity in the low end of phosphorous concentration and has a similar capacity as the KOH activator at the high end of phosphorous concentration where both products will seek the same values since that is determined by lanthanum content which is the same in both products.

Preferred Method of Lanthanum addition

As mentioned in the Activity 1 final report, considerable effort was expended to determine the best method for attaching lanthanum to the hydrochar. **In-situ** addition consists of adding the lanthanum and activating agent (base) to the HTC reactor along with the biomass plus water and subjecting the combined contents to HTC processing. With this method, the lanthanum construct tends to be uniformly distributed throughout the hydrochar particles. However, there is always some unattached lanthanum remaining in the residual liquid phase (filtrate). This is a concern from an economic standpoint and more importantly also presents engineering problems with recovery and /or recycle of the residual lanthanum. An alternative is to add the lanthanum and activating base to the hydrochar **in a post addition** second step outside of the reactor after the hydrochar is formed through HTC processing of the biomass alone. This **post addition** offers operational, economic and environmental advantages:

- **In-situ** lanthanum addition requires an expensive glass liner inside the reactor to mitigate corrosion from the strong base (KOH) and would need to be replaced frequently at considerable cost. **Post addition** requires no glass liner.
- There would be no Lanthanum in the HTC reactor filtrate to recover or remediate which **minimizes Lanthanum cost and avoids remediation to avoid any discharge of lanthanum to the environment.**

Kinetic data for post vs. in-situ lanthanum addition are illustrated below:
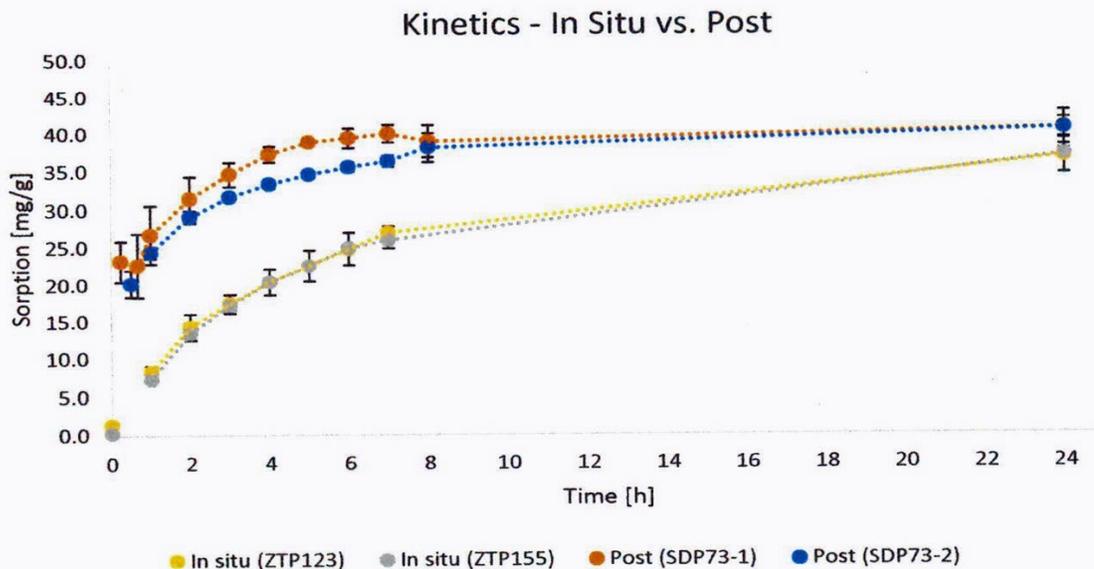
Kinetic curves for hydrochar with in situ addition (ZTP123 and ZTP155), hydrochar with post addition (SDP73-2) and biochar with post addition (SDP73-1). The two upper curves are for post addition and the two lower curves are for in-situ addition.

Post addition of lanthanum produces faster binding of phosphorous (Fig. 1). However, phosphorous binding capacity is expected to be essentially the same for post and in-situ addition of lanthanum since the lanthanum content of the two alternatives is the same. Within the first 30 min over 40% of the available phosphorus was removed from a solution of 25ppm phosphorous. For this treatment hydrochar (SDP73-2) and biochar (SDP73-1) were treated with $La(NO_3)_3$ and KOH. Available lanthanum is deposited directly onto the surface of the hydrochar. In situ hydrochars were produced at 225 ºC and differed only in caustic bases used in the HTC process: i (ZTP123 with NaOH) and ii (ZTP155 with KOH). Therefore, the decision was made to focus on **post addition of lanthanum** to the char after hydrothermal carbonization (HTC) of the biomass **instead of in-situ addition** during HTC of the biomass/lanthanum cocktail.

Multiple tests were performed with corn stover as the biomass source as well as other support materials including sand, zeolite and a high surface area carbon black (BP2000, Cabot corp.). Specific biomass material variations were raw corn stover, corn stover with post thermal treatment (PTT), cornstover with hydrothermal carbonization (HTC) treatment, corn stover with HTC plus PTT and beef manure with HTC plus PTT. The chemical additives were lanthanum nitrate, $La(NO_3)_3$ and sodium hydroxide (NaOH). Phosphate removal ranged from 24.8-45 mg phosphorus /gram char

Experimental Procedure

A 24- hour batch equilibrium phosphate removal test was conducted to evaluate the capacity of the hydrochars to remove phosphate from water. A small sample of bio-hydrochar composite is combined

with a 50ppm PO4-P challenge solution and mixed for 24 hours. At the conclusion of the mixing period the solid material is filtered out of the solution and the amount of phosphorus remaining in solution is measured. Once the ending phosphorus concentration is determined the capacity of the composite to remove phosphate from solution can be calculated. This capacity is then normalized to the units of mg phosphorus removed per 1 gram of composite. The capacity for a material to remove phosphorus from water is the key performance parameter. All the chars tested contained between 23-24% lanthanum by weight.

The major observations from a 50ppm phosphate test solution were: (The raw data are listed in the table below)

- Phosphorus removal ranged from 25-45 mg phosphorus /gram char
- PTT of corn stover doubled the removal rate over a 24 hr. period
- HTC plus PTT of corn stover gave similar results as simple PTT of stover
- Zeolite and BP2000 removed 40.0 and 44.5 mg phosphorous/ gram of doped support respectively
- Sand removed only 13mg phosphorus/ gram of doped support

Both zeolite and BP2000 would be expensive support materials compared to the variations of corn stover or manures. It should be noted that these are 24 -hour removal values. All samples contained the same amount of lanthanum so it is reasonable to expect that over a much longer observation time the samples would likely asymptotically approach the same removal capacity. However, in a flow situation, such as flow in a draintile, the rate of removal is an important consideration.

Raw data for phosphorus removal from 50ppm challenge solution

Lanthanum Post Addition Overview - 12/14/17

Char ID	Lanthanum Compound	Base	Char Description	Char I.D.	Stover Conversion	La added (mg)	La in filtrate (ppm)	La in wash 1 (ppm)	Est. La on char (mg)	% La on Char (%)	Char yield (mg)	Char wt% La (wt%)	initial conc. (ppm PO4-P)	sorption (mg PO4-P/g char)	Filter Time (Wash 1) (minutes)
SDP73-2	La(NO3)3	KOH	L.T. HTC Stover	ZTP2-41	0.46	348	523	9	321	92	1290	25	50	34.3	9
RN47	La(NO3)3	KOH	L.T. HTC Stover	ZTP2-71	0.33	348	100	23	342	98	1410	24	50	37.6	30
SDP116	La(NO3)3	KOH	L.T. HTC Stover	ZTP2-71	0.33	348	143	62	338	97	1390	24	50	41.3	75
SDP114	La(NO3)3	NaOH	L.T. HTC Stover	ZTP2-71	0.33	348	304	53	330	95	1380	24	50	27.5	54
RN40	La(Cl)3	KOH	L.T. HTC Stover	ZTP2-71	0.33	348	149	46	338	97	1380	25	50	20.8	66
RN17	La(NO3)3	KOH	Raw Stover	NA	1.00	348	147	8	340	98	1390	24	50	24.8	48
SDP118	La(NO3)3	KOH	H. T. (250) HTC Stover	ZTP2-83	0.37	348	56	66	342	98	1430	24	50	25.3	140
RN7	La(NO3)3	KOH	HTC La in situ	ZTP2-35	0.54	648	448	466	602	93	1420	42	50	42.5	124
SDP 135	La(NO3)3	KOH	L.T. HTC Stover	ZTP2-81	0.44	696	127	206	679	98	1880	36	50	38.2	148
SDP 136	La(NO3)3	-	LT Stover MgCl2 in situ	ZTP2-62	0.34	348	2491	407	203	58	940	22	50	0.0	1
SDP 137	La(NO3)3	KOH	LT. stover (new)	ZTP2-81	0.44	348	81	108	339	97	1500	23	50	24.0	165
SDP73-1	La(NO3)3	KOH	Raw Stover->PTT (900)	ZTP2-42-1	0.24	348	300	0	333	96	1370	24	50	44.5	2
SDP 149	La(NO3)3	KOH	Raw Stover->PTT (600)	ZTP2-128-3	0.29	348	0	9	348	100	1480	23	50	43.3	19
RN11	La(NO3)3	KOH	HTC La in situ ->PTT (600)	ZTP2-39-3	0.38	668	1838	564	548	82	1080	51	50	34.6	84
RN15	La(NO3)3	KOH	HTC Stover ->PTT (600)	ZTP2-39-2	0.21	174	143	121	161	92	700	23	50	34.8	49
SDP126	La(NO3)3	KOH	LT Stover ->PTT (600)	ZTP2-95-1	0.22	348	14	0	347	100	1490	23	50	43.3	20
SDP127	La(NO3)3	KOH	HT Stover ->PTT (600)	ZTP2-95-2	0.21	348	0	0	348	100	1490	23	50	42.9	7
SDP 150	La(NO3)3	KOH	LT Stover ->PTT (600)	ZTP2-128-1	0.19	348	27	9	347	100	1490	23	50	45.1	11
UG30	La(NO3)3	KOH	BP 2000	NA	NA	348	9	NA	348	100	1510	23	50	44.5	17
SDP123	La(NO3)3	KOH	Sand	NA	NA	348	-	-	-	-	1440	-	50	13.2	1
SDP 142	La(NO3)3	KOH	zeolite (expensive)	NA	NA	348	16	105	347	100	1360	26	50	40.5	170
SDP 154	La(NO3)3	KOH	beef manure HC	ZTP 96	NA	174	37	53	172	99	750	23	50	24.2	91
SDP 155	La(NO3)3	KOH	beef manure HC then PTT	ZTP 112-3	NA	174	17	22	173	100	730	24	50	30.8	9

Terms:

"stover conversion" refers to the mass of char product remaining after either HTC or PTT processing. For example a conversion of 0.5 means 1g stover yields 0.5g char

"% La on char" refers to the percentage of lanthanum that is deposited onto the char out of all the lanthanum put into the process. Estimated based on the La measured in filtrate and washes

43

Phosphate Sorption Isotherm Test with Post Added Lanthanum Chars

The results of an isotherm test with 5 starting phosphate concentration points are consistent with previous results for these four stover based materials with post add lanthanum. Specifically, the two chars that received PTT, SDP 127 and SDP 149, had higher phosphate removal across the range of concentrations during this 24 hour batch equilibrium removal test. Also note that for the raw stover starting material and hydrochar starting material, (RN 17 and SDP 118), removal was also consistent with the 24-hr.batch equilibrium tests.

For each sorption (removal) isotherm shown below the char was tested against solution with starting concentrations of 30, 40, 50, 60, and 70 ppm PO4-P

Phosphate Sorption Isotherm Results:
Comparison of Four Stover Materials with Lanthanum Post Addition
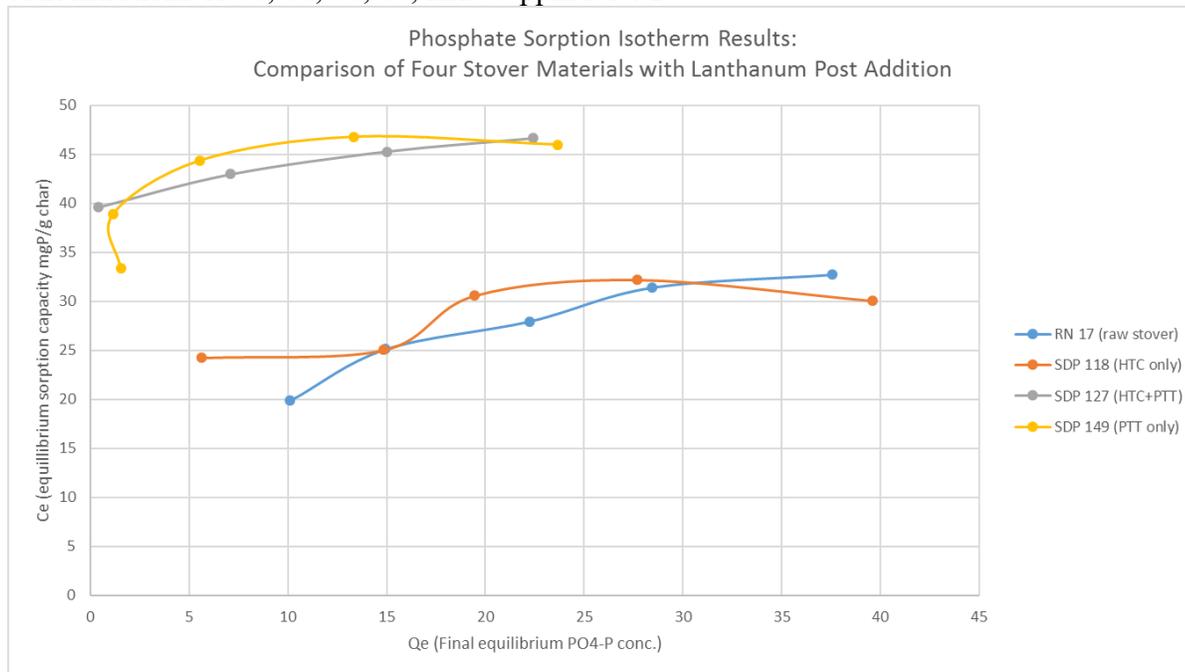
Specific Char information, lanthanum tracking, P sorption at 50ppm starting conc. and filter time

Char and Chemical Addition Information			Lanthanum		P Sorption			Other Info
Char ID	Char Description	Stover Conversion	% La on Char	Char wt% La	initial conc.	sorption		Filter Time (Wash 1)
			(%)	(wt%)	(ppm PO4-P)	(mg PO4-P/g char)		(minutes)
RN17	Raw Stover	1.00	98	24	50	24.8		48
SDP118	H. T. (250) HTC Stover	0.37	98	24	50	25.3		140
SDP 149	Raw Stover->PTT (600)	0.29	100	23	50	43.3		20
SDP127	HT Stover(250)->PTT (600)	0.21	100	23	50	42.9		7

Impact of HTC

If the biomass of choice is corn stover, then HTC processing does not increase the removal rate over simple PTT. In the case of corn stover it is an unnecessary complication. HTC of stover produces a **hydrochar**. Subsequent PTT treatment converts the hydrochar to a **bio-hydrochar**. Conversely, PTT treatment of raw corn stover results in a **biochar**. ***Bio-hydrochar is different than either biochar or hydrochar in its physical properties and chemical structure.***

On the other hand, if the biomass of choice is a wet dilute slurry such as manure or municipal waste treatment sludge, **then HTC is a necessary and beneficial step** in converting the slurry to a solid capable of being a carrier or support structure for lanthanum.

Bio-hydrochars (HTC+PTT) made from cattle, poultry and swine manures, as well as corn stover were exposed to a 50 ppm phosphate test solution and removal capacity over a 24 hr. period was measured. Results are illustrated in the table below.

Phosphorus Removal Capacity of bio-hydrochars

Starting Biomass	Starting P Conc.	Ending P Conc.	Phosphorus Removal Capacity
units	ppm PO_4-P	ppm PO_4-P	(mg PO_4-P)/(g material)
Corn Stover	50.0	6.7	43.3
Cattle Manure	50.0	7.8	42.3
Poultry Manure	50.0	17.9	32.0
Swine Manure*	50.0	15.6	34.4

*Swine manure hydrochar requires an intermediate acid washing step before PTT to be effective because swine hydrochar contains a high level of phosphorus when the manure is processed via HTC. This must be removed for the subsequent lanthanum addition to be effective.
All four materials achieved phosphorus removal in the range of 32 - 43 mg of phosphorus per gram of composite. The materials derived from corn stover and cattle manure were found to be the most effective with these test conditions as they each reached a removal capacity of greater than 40 mg P per gram composite material. For comparison, raw corn stover impregnated with lanthanum and exposed to the 50 ppm challenge solution will sequester 25mg phosphorus / gram material in the 24-hr period.

Surface Modification

Both HTC and PTT modify the surface structure and physical properties of biomass such as corn stover. This is illustrated in the table below for the case of lanthanum impregnated raw stover and one that has had HTC and PTT treatment. The surface modified bio-hydrochar stover reaches equilibrium in 24 hrs. or less. Whereas the raw stover has not reached equilibrium even after 168 hours of contact even though both substrates have the same amount of lanthanum. It appears that the surface modification caused by HTC and/or PTT present the lanthanum more readily to the phosphorous in the challenge solution than the raw stover based material. This would be an important consideration in a flow application such as in draintiles.

Approach to Equilibrium

Treatment	Contact time	% P removed from solution
None raw stover	24 hr.	50.

None raw stover	168 hrs.	67.5
HTC + PTT	24 hrs	87
HTC + PTT	168 hrs.	87

Phosphorus removal mechanism with Lanthanum.

Lanthanum is a rare earth element that is particularly effective in sequestering phosphates from aqueous solution by forming a highly insoluble precipitate, lanthanum phosphate. It has been shown to be effective in removal of phosphate from municipal waste treatment effluent and is most active in the pH range typically found in agricultural runoff waters (Recht,1970). The challenge is to present the lanthanum to phosphate containing waters in a matrix that will effectively remove phosphate and have a relatively high holding capacity for phosphate. At the same time the matrix should be stable and retain the lanthanum phosphate for subsequent recovery and recycle of both lanthanum and phosphate.

Lanthanum (III) has been shown to be more effective than Al(III) for precipitation of phosphates across a broader pH range. In studies with orthophosphate the removal of phosphate is stoichiometric with lanthanum. This suggests "a purely chemical reaction between the lanthanum and orthophosphate and not through adsorption (chemical or physical) of phosphate on a precipitated metal hydroxide". Orthophosphate is an end-product of the microbial degradation of phosphorous containing organic compounds. O-phosphate is the form most readily available for biological utilization. Lanthanum was found to be most effective in the pH range of 4 to 9 with optimum at 5. (Recht, 1970).

A commercial product, **Phoslock®,** is the reaction product of bentonite or equivalent clay with lanthanum chloride in a substitution process in which most of the sodium in the bentonite is replaced by lanthanum, with variable substitution at other sites for elements such as calcium and magnesium. It was developed in the 1990's by the Australian national science agency, Commonwealth Scientific and Industrial Research Organization (CSIRO), to remove phosphorus from water bodies and restore water quality**. It is designed to be used in quiescent waters such as ponds, lakes and reservoirs. It would not be very effective in a flow situation such as a drain tile or in surface runoff.**

Recht, Howard and Masood Ghassemi, Federal Water Administration, Department of the Interior, Program #17010, Advanced Water Treatment Research, (1970)

Potential Leaching of Lanthanum into draintile waters

Lanthanum is "attached" to or coated onto the char carrier as lanthanum hydroxide. When it is contacted by water containing phosphates it forms a highly insoluble precipitate of lanthanum phosphate. This situation raises two questions.

1.**How tenaciously does lanthanum hydroxide adhere to the char?** Does it get leached from the char carrier when exposed to water flowing in the draintile?

2. **Does the insoluble lanthanum phosphate stay "attached" to the** char carrier or is it released to the water stream?

 Leaching tests were conducted over a 24 -hour period in an agitated vessel with water on a variety of chars that could be utilized as carriers for lanthanum hydroxide. The amount of lanthanum lost to leaching was about 3% or less for corn stover based chars. Longer tests were not feasible because the

agitation begins to disintegrate the char and confound the lanthanum measurements. It is expected that this 3% loss will not increase very much for longer times as it is suspected that what is leached from the coated carrier represents lanthanum hydroxide that is loosely bound since the leaching is due to hydrodynamic friction at the water-solid interface rather than some sort of equilibrium relationship. Any lanthanum hydroxide in the tile water will come in contact with phosphate and be removed from the stream as a highly insoluble precipitate of lanthanum phosphate becoming biologically inactive..

Tests were conducted several times to determine **if any significant amount of lanthanum phosphate was released by the char** into the water phase. Any potential insoluble lanthanum phosphate was isolated from the char-water mixture by selective filtration. This material was acidified at pH<2 to hydrolyze the lanthanum and phosphate components to submit for ICP analysis by an independent laboratory (KMT, Keystone materials testing) to determine if any lanthanum could be detected. **Results from KMT and our internal measurements with a Hach Spectrophotometer indicated amounts of <1ppm. The lanthanum phosphate appears to be tenaciously held in place by the char carrier. The mechanism by which it is bound to the char is not clear.**

Conclusions:

- Post addition of Lanthanum preferred method of incorporation to char
- Removal mechanism is formation of highly insoluble precipitate of Lanthanum phosphate
- No significant amount of lanthanum phosphate detected in leachate water
- PTT surface modification of chars increases removal rate but not ultimate phosphorus removal capacity
- La modified chars made from most manures as effective as corn stover constructs
- Phosphorus removal from 50 ppm solution was in range of 25-45mp P/gram modified char.

Outcome 1 was completed.

Outcome 2 was not completed since the determination of the sorption indices for the hydrochar and soil additions were not successful since the hydrochar would separate from the soil addition during the laboratory shaking. This resulted in a lack of the representative nature of the laboratory batch study. The results for the raw materials were used for P sorption discussion.

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:	$ 159,807
	Balance:	$ 0

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, 2018
2. Desorption experiments on "best" candidates from sorption studies. (start date June 1, 2016)	May 31, 2018
3. Incineration studies with analysis of combustion exhaust gases.	May 31, 2017
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, 2018

Activity Status as of *[July 30, 2016]***:***]***:**
Radio-labeled pesticides have been obtained for the sorption experiments, and staff have been trained in the
radioisotope handling and standard operating procedures (SOP). To date, 33 hydrochars prepared from 7
different biomass feedstocks and various production alternatives have been initially screened across the four
pesticide chemicals classes listed above. Although data analysis is still in the initial phases, the dependency on
post-production conditioning appears to have a greater influence than feedstock variety.   Desorption
experiments have been initiated and data is currently being collected across the various HTC materials from
Activity 1.
Soils that will be used in these experiments have been collected from across Minnesota: Rosemount, Staples,
Morris, and Becker.

Activity Status as of *[Dec. 31, 2016]***:**
The actual pesticides used in these experiments differ from those originally listed because of the need to have pesticides that are 14-C labelled to be able to easily detect them at low concentrations with acceptable accuracy. The pesticides utilized still represent major chemical classes used in Minnesota.
They are;

Pesticide Tested	Chemical Class
Alachlor, Metolachlor	chloroacetanilide
Imazethapyr	imidazolinone
Imidacloprid	neonicotinoid
Diketonitrile	isoxazole
Glyphosate	organophosphate

Further experiments were carried out evaluating the capacity of various hydrochars to adsorb a radio-labeled pesticide from the neonicotinoid class, which has become an environmental concern in recent years following links to declining bee populations. The newly collected neonicotinoid data completes the screening phase of the 33 hydrochar series for pesticide adsorption. Through this screening, we have observed that for all 5 pesticide chemical classes tested, post production conditioning has a greater impact than feedstock variety on sorption capacity on an equivalent mass basis. Post production conditioning consists of heating hydrochar to high temperature in an inert gas atmosphere for a time sufficient to increase porosity and surface area by two or more orders of magnitude. A subset of hydrochars was selected based on adsorption performance, and isotherm analysis and kinetics testing have been initiated. Based on initial data, desorption experiments have been delayed to take place following maximum sorption capacity experiments. Therefore, desorption experiments initiated at the time of the previous report have been temporarily suspended and the focus is currently on maximizing the pesticide sorption capacity of the hydrochars.

Preliminary testing has been performed to determine if a hydrochar designed for phosphate sorption could simultaneously adsorb the herbicide glyphosate, an organophosphate. This herbicide has the highest application rate in lbs/year in Minnesota as reported by the MN dept. of agriculture. From these initial tests we have observed that the hydrochar's capacity to remove glyphosate from solution is not significantly reduced in the presence of phosphate and this specific engineered hydrochar is capable of capturing phosphate and glyphosate simultaneously. An invention disclosure on this discovery has been submitted to the Office for Technology Commercialization of the University of Minnesota on 12/09/16.

Activity Status as of *[July 30, 2017*

A subset of hydrochars was selected based on pesticide adsorption performance and additional testing has been initiated on this smaller set including kinetics testing and small- scale column sorption testing. As reported in the last update it has been determined that post production conditioning has a greater impact on sorption capacity than feedstock variety. To further investigate this initial finding, the kinetics testing and column testing has included hydrochars with post production conditioning. Previous testing has focused on the total capacity of hydrochars to adsorb pesticide, but not on the rate of adsorption which is also an important factor. Both kinetics testing and column sorption testing yield important information about this rate. To measure the increase in hydrochar surface area as a result of post-production conditioning, tests utilizing various saturated salt solutions have been initiated. While these are somewhat time consuming they are considered to be accurate and are much less expensive than traditional BET testing.

Further experiments have been conducted to follow up on initial results with a hydrochar to simultaneously adsorb phosphate and the herbicide glyphosate (Roundup^R) from water. These results have clarified the specific production conditions required to achieve the adsorption of both chemicals. An updated report has been submitted to the Office for Technology Commercialization of the University of Minnesota and they have **committed to a provisional patent filing**.

Activity Status as of *[Dec. 31, 2017]*:

Small scale column testing

Work continues to identify hydrochars with the highest capacity to remove pesticides from aqueous solutions, with a particular focus on the neonicotinoid insecticide Imidacloprid. Since the last update, preliminary surface area measurements have confirmed that post production conditioning results in a higher surface area material and a limited **small-scale column** study has been completed with selected hydrochars. The response of the hydrochars in the columns is more representative of performance in a field application versus previously completed equilibrium sorption testing.

The **small-scale column** test procedure consists of mixing a small hydrochar sample with sand to increase column bed volume for testing. The mixture is loaded into a plastic syringe, which serves as the column. A specific volume of solution containing radiolabeled pesticide is added to the loaded column and allowed to pass through gravimetrically. The solution which passes through the column is collected and analyzed for pesticide content. Then the amount of pesticide captured by the hydrochar can be calculated.

Small-scale column results for hydrochar sorption performance are consistent with equilibrium sorption results, and the best performing hydrochars have been identified. More extensive small-scale column testing will be completed along with additional analysis methods for sorption rate and maximum sorption capacity in the coming months to complete a comprehensive summary of pesticide sorption performance.

Finally, a series of runs with the inert gas furnace was performed to study the reproducibility of the process, and to establish the variability of pesticide sorption performance of a given hydrochar. This study was required before moving on to final hydrochar sorption assessment, which is now underway as discussed above.

Pesticide Reproducibility Study

Three hydrochar replicates were produced to investigate the extent to which pesticide sorption performance is consistent from batch to batch. The biomass feedstock used for this study was corn stover that underwent hydrothermal carbonization treatment for 4 hours at 250°C. The resulting char was then post thermally treated in an inert gas furnace to produce a high surface area product, and was labelled sample ZTP2-109. This process was then repeated with 2 more hydrothermal carbonization treatments followed by post thermal treatment to produce two replicate samples, labelled ZTP2-112 and

ZTP2-114. The following table details imidacloprid pesticide sorption performance of these three hydrochars. For each char, a triplicate sorption run was performed, the average percent of imidacloprid sorbed from solution is reported along with the standard deviation within the triplicate run. The results show that variability in performance between hydrothermal carbonization and thermally treated batches is very low.

Char I.D.		% Imidacloprid Sorption	Average Sorption within Triplicate	Standard Deviation within Triplicate
ZTP2-109		97.37	97.31	0.055
ZTP2-109		97.27		
ZTP2-109		97.28		
ZTP2-112		97.29	97.31	0.072
ZTP2-112		97.25		
ZTP2-112		97.39		
ZTP2-114		97.28	97.32	0.047
ZTP2-114		97.37		
ZTP2-114		97.30		

Glyphosate
The university filed a provisional patent entitled, METHOD FOR REMOVING AN ORGANOPHOSPHOROUS COMPOUND FROM AN AQUEOUS MEDIUM, on Dec. 11, 2017.

Final Report Summary: July 30, 2018

LCCMR Final Report Activity 4: Pesticide **Sorption July 30, 2018**
Introduction:
The effective production of food and fiber relies on pesticides to control weeds, insects, and plant diseases that interfere with the growth, harvest, and marketability of crops. In the fields, pesticides do an important job for the farmer, but when they run off into surface or groundwater they can pose a threat to water quality and raise environmental issues. The impact of pesticides on water quality' is a technically complex subject.
The objective of this research was to determine if an engineered hydrochar, fabricated from inexpensive agricultural residues, would remove pesticides from agricultural drainage waters. Pesticides include chemicals such as insecticides, herbicides, fungicides and others. In this study the effort was focused on herbicides and insecticides that are frequently used in Minnesota.

Initial screening experiments

The physical property of various hydrochars to capture pesticides from water was first examined with a broad set of screening experiments. The pesticides used in the screening study represent major chemical classes used in Minnesota and are listed in Table1. The effectiveness of various hydrochars to capture each of the six pesticides of interest, which is displayed as the percentage of the respective pesticide removed from a water sample, is illustrated in table 2. These hydrochars were produced from a variety of inexpensive and widely available agricultural residues including corn stover, an ethanol production by-product called condensed distillers solubles (CDS), swine manure, poultry manure, beef cattle manure, and peat.

Table 1. Pesticides used for screening study

Pesticide Tested	Chemical Class
Alachlor, Metolachlor	chloroacetanilide
Imazethapyr	imidazolinone
Imidacloprid	neonicotinoid
Diketonitrile	isoxazole
Glyphosate	organophosphate

Experimental Methods:

The propensity of materials, including hydrochar and biochar, to remove pesticides from water was determined by monitoring their concentration in solution during controlled experiments. A known amount of pesticide chemical is added initially along with the material of interest to a vessel. Depending on the specific test a certain amount of time is allowed for the water and material to interact. Then a sample of the water is taken to determine the new concentration of pesticide. If the material was effective the concentration of pesticide in water is reduced. Finally, the amount of pesticide removed is normalized by the mass of sorbent material used. This calculated value is the capacity of the material to remove the pesticide from water and the key performance metric.

Radiolabeled pesticide chemicals were utilized in order to precisely measure the concentration of pesticide in water. Starting concentrations and final concentrations which were used as described above were obtained by employing a liquid scintillation counter in conjunction with the radiolabeled pesticides.

From these screening experiments, it was observed that for all 5 pesticide chemical classes tested, post production thermal treatment(PTT) of the sorbent material has a greater impact than feedstock (biomass) variety on sorption capacity on an equivalent mass basis. PTT consists of heating hydrochar or solid biomass material to high temperature ($\sim600^0$C) in an inert gas atmosphere for a time sufficient to modify the surface chemistry. It is not clear whether this actually increases the char surface area or modifies the functional groups affecting surface chemistry. But regardless, PTT changes the char or biomass in such a way as to render it more likely to sorb organic chemicals such as pesticides.

The relative importance of HTC and PTT treatment is not clear, as indicated at least anecdotally, from these data. HTC is necessary for any biomass source that is in the form of a slurry such as the manures to obtain an actual char. Manures contain at least 90% water and it would be costly to dry this material to obtain a solid that would be useful as a sorbent. Without subsequent PTT these chars are not very effective sorbents. However, while PTT improves the sorption capacity of poultry and cattle manure hydrochars appreciably it does not do so for swine manure hydrochar. For corn stover, which is a solid biomass material, PTT alone renders it a good sorbent. On the other hand, for peat it is necessary to first

use HTC followed by PTT to get a good sorbent. BP 2000, a very pure carbon black with high surface area (Cabot Labs), was used as a control as it is an excellent sorbent for all the pesticide classes except glyphosate. It is also very expensive compared to the agricultural residue chars.

Note that there remains significant uncertainty of the particular mechanism which is responsible for the observed ability of modified hydrochar and biochar materials to remove pesticides from water. The results in this and following sections do not closely follow established sorption models. Therefore, it cannot be concluded that the materials remove pesticides from water by way of sorption. In the context of this report "sorption" means removed or sequestered from solution.

Table 2. Pesticide sorption screening experiments

Pesticide sorption summary

				Results - % sorbed for respective pesticide green highlight if >75%, yellow if between 50% and 75%					
ID #	Notebook ID	Feedstock	Treatments Applied	alachlor	imazethapyr	metolachlor	DKN	glyphosate	Imidacloprid
NA	ZTP-89	CDS	HTC, 225C	49	3	51	13	-5	25
HC-11	ZTP 34	CDS	Acid/base washed, HTC	58	7	65	9	-2	27
HC-12	ZTP 34	CDS	Acid wash, NaOH neutralized, HTC	57	6	67	31	-1	-
HC-25	ZTP 60-2	CDS	HTC, PTT	75	43	84	45	18	65
NA	BC299	Stover	Raw, no treatment	15	3	25	5	-3	11
NA	ZTP 80	Stover	225 HTC	20	6	21	8	0	16
HC-31	ZTP 82	Stover	High temp HTC	23	7	32	5	5	16
NA	ZTP 112-1	Stover	PTT	91	53	97	49	20	94
HC-32	ZTP 86-1	Stover	HTC, PTT	96	87	85	73	73	96
HC-33	ZTP 86-2	Stover	HTC, PTT, KOH in situ	97	95	91	93	93	97
HC-34	ZTP 86-3	Stover	High Temp HTC, PTT	87	49	88	47	47	65
HC-23	Raw Peat	Peat	Raw, no treatment	42	12	50	7	67	42
NA	ZTP-56	Peat	HTC 225C, 2hr	39	4	67	6	8	40
NA	ZTP-91	Peat	PTT	47	20	54	23	13	74
HC-24	ZTP 60-1	Peat	HTC, PTT	93	75	91	77	52	94
HC-5	MNK 92	Swine	HTC, wash no acid no acetone	39	4	48	8	1	-
HC-6	MNK 92	Swine	HTC, wash acid no acetone	47	39	47	49	2	-
HC-7	MNK 92	Swine	HTC, wash acid and acetone	54	54	67	55	3	37
HC-27	ZTP 60-4	Swine	HTC, PTT	57	60	77	29	10	32
HC-28	ZTP 60-5	Swine	HTC, acid wash, PTT	57	49	70	14	9	24
HC-1	6-207-1	Poultry	HTC, Acid extracted	52	54	63	39	5	-
HC-19	ZTP 50	Poultry	HTC, acid washed	53	26	63	58	3	-
HC-30	ZTP 51	Poultry	HTC, no wash	28	6	32	10	10	15
HC-26	ZTP 60-3	Poultry	HTC, PTT	76	66	88	49	85	84
NA	ZTP-96	Beef (finisher)	HTC	26	3	32	9	2	34
NA	ZTP-103	Beef (grower)	HTC	25	4	27	5	1	20
NA	ZTP 112-3	Beef (finisher)	HTC, PTT	72	70	82	54	14	86
NA	ZTP 112-4	Beef (grower)	HTC, PTT	82	84	92	69	7	93
HC-20	BP 2000	BP2000	NA	94	95	97	99	70	93
HC-2	SMH2-112-2	Algae	HTC	27	8	29	10	6	20
HC-3	SMH2-151-2	Muni Crude Waste	HTC	37	23	50	10	16	21
HC-8	6-23-3	Muni Waste	HTC, Acid and acetone washed	46	44	49	30	24	39
HC-4	JM-13.9.5-2	Cheese Whey	HTC	5	5	7	0	22	7

HTC = a hydrochar made by hydrothermal carbonization
PTT = a biochar or a bio-hydrochar made by post thermal treatment of biomass or hydrochar at high temperature in an oxygen free atmosphere.
The best hydrochars are highlighted in yellow if sorption was between 50-75% and in green if sorption was>75%

Glyphosate and phosphate simultaneous sorption/removal

Glyphosate is an organophosphate compound, which is used as a non-selective herbicide in agriculture. The Minnesota Department of Agriculture reports that in 2011 farmers purchased 24.5 million pounds of glyphosate (R1). At 24.5 million pounds it is the most purchased by a large margin, with the next highest purchased crop chemical at 6 million pounds. Concern about glyphosate has been increasing. For example, a recent report from the World Health Organization in 2015 reached the conclusion that glyphosate is probably carcinogenic to humans (R2). Partially based on this finding California is currently in the process of labelling glyphosate as "known to the state to cause cancer" (R3). Around the world, research continues to assess the potential harmful effects of glyphosate on human health, wildlife, and non-target plants.

Tests were conducted to determine if a lanthanum modified hydrochar designed for phosphate sorption could simultaneously adsorb the herbicide glyphosate, an organophosphate. A significant concern is that the capacity of a biochar or hydrochar to sorb glyphosate from water will be significantly reduced through competitive sorption of phosphate which might also be present in the water. When glyphosate is removed from water by an active biochar or hydrochar it attaches to a sorption site through its phosphate moiety. These sites also attract phosphate, which is present in agricultural waters in higher concentrations than glyphosate, and research has shown phosphate will out-compete glyphosate to occupy these sites (R4). Since phosphate is preferentially sorbed to these sites, the presence of phosphate in agricultural waters would prevent effective glyphosate removal by biochars and hydrochars. The question was whether a lanthanum modified hydrochar would neutralize this complication and simultaneously sorb phosphate and glyphosate in significant quantities.

Simultaneous sorption phenomenon

The experiments (table 3) yielded the surprising result that the lanthanum modified hydrochar could sorb a significant amount of glyphosate from the solution, and that the presence of excess phosphate resulted in only a small reduction in sorption capacity. Specifically, the hydrochar sorbed 0.80mg glyphosate per gram hydrochar without phosphate present versus 0.71mg glyphosate per gram hydrochar in the presence of phosphate. The second result, 0.71mg, was in water which had a phosphate concentration of 13ppm remaining. Based on previous research it would be expected that the excess phosphate in solution would replace the glyphosate and reduce the glyphosate sorption to zero. That was not the result in this experiment, which indicates that the mechanism of glyphosate sorption is simultaneous and essentially non-competitive with phosphate sorption.

Table 3: Simultaneous Glyphosate and Phosphate Sorption Results for La+KOH Treated Corn stover Hydrochar

Run Description	Initial phosphate concentration	Final phosphate concentration	Initial glyphosate concentration	Final glyphosate concentration	Total glyphosate sorption
units	ppm PO4-P	ppm PO4-P	ppm glyphosate	ppm glyphosate	% (mg/g)
Glyphosate only	0	0	1.0	0.20	80 (0.8)
Glyphosate and phosphate	30.0	12.9	1.0	0.29	71 (0.71)

The capacity of each hydrochar or biochar to adsorb glyphosate is reported in the far -right column as percent of glyphosate removed from solution (%) and additionally as the mass captured normalized by the mass of hydrochar/biochar used. (mg glyphosate / g hydrochar or g biochar) or (mg/g)

Conclusions for Glyphosate

This corn stover derived modified hydrochar appears to have a unique and unexpected capacity to simultaneously adsorb phosphate and glyphosate from water, as demonstrated by the experiments outlined above.

Similar experiments with a corn stover derived biochar, rather than a hydrochar, indicate that the lanthanum and potassium hydroxide post addition treatment is also effective for biochar, table 4

Table 4: Glyphosate Sorption Capacity of a Corn Stover derived Biochar with and without Lanthanum in solution with 30ppm PO4.

Biochar Description	Metal used	Base used	Initial glyphosate concentration	Final glyphosate concentration	Total glyphosate sorption
units	-	-	ppm glyphosate	ppm glyphosate	% (mg/g)
Biochar from Stover	-	-	1.0	0.62	40 (0.04)
Biochar from stover, with Lanthanum+KOH addition	Lanthanum	KOH	1.0	0.13	87 (0.87)

The Office for Technology Commercialization of the University of Minnesota has filed a provisional patent. entitled, **METHOD FOR REMOVING AN ORGANOPHOSPHORUS COMPOUND FROM AN AQUEOUS MEDIUM**

Glyphosate references:

R1: MN dept. of agriculture chemical purchase information http://www.mda.state.mn.us/chemicals/pesticides/useandsales.aspx
R2: IARC Monographs Volume 112: evaluation of five organophosphate insecticides and herbicideshttp://www.iarc.fr/en/media-centre/iarcnews/pdf/MonographVolume112.pdf
R3: Notice of intent to list … glyphosate. Office of Environmental Health Hazard Assessment https://oehha.ca.gov/proposition-65/crnr/notice-intent-list-tetrachlorvinphos-parathion-malathion-glyphosate
R4: Effects of phosphate on the adsorption of glyphosate on three different types of Chinese soilshttps://www.ncbi.nlm.nih.gov/pubmed/16312989

Neonicotinoid Pesticides

Through the screening experiments it was observed that for all 5 pesticide chemical classes tested, post production treatment has a greater impact than feedstock variety on sorption capacity on an equivalent mass basis. To reduce the number of experiments to a manageable level it was decided to **focus on corn stover as the single biomass source**. This was driven by its availability, relative consistency in composition, low cost and significant convenience in handling when compared to wet, noxious slurries such as manures or municipal sewage sludge.

Additionally, since radio-labelled pesticides are quite expensive and the testing of pesticide sorption is time consuming, the number of pesticides considered for more in-depth testing needed to be reduced to a reasonable number. **Glyphosate was one** of those selected because of its wide use in Minnesota agriculture. The other was **imidacloprid, a neonicotinoid** pesticide of interest. The neonicotinoid class has become an environmental concern in recent years following alleged links to declining bee populations.

Comparison of Four Stover Based Materials for Imidacloprid Sorption Capacity
Because PTT chars were made in a batch oven it was important to establish that this method of PTT was reproducible and providing consistent results.

Reproducibility Study
Three materials were produced to investigate the extent to which pesticide sorption performance is consistent from batch to batch. The biomass feedstock used for this study was corn stover. A certain amount of stover was taken and underwent hydrothermal carbonization treatment for 4 hours at 250°C. The sample was then post thermally treated in an inert gas furnace to produce a high surface area product and was labelled sample ZTP2-109. This process was then repeated with 2 more hydrothermal carbonization treatments followed by post thermal treatment to produce two replicate samples, labelled ZTP2-112 and ZTP2-114. The following table details imidacloprid pesticide sorption performance of these three hydrochars. For each char a triplicate sorption run was performed, the average percent of imidacloprid sorbed from solution is was reported along with the standard deviation within the triplicate run. The results in Table 5 show that variability in performance between batches is very low.

Table 5. Results of reproducibility testing

Char I.D.		% Imidacloprid Sorption	Average Sorption within Triplicate	Standard Deviation within Triplicate
ZTP2-109		97.37	97.31	0.055
ZTP2-109		97.27		
ZTP2-109		97.28		
ZTP2-112		97.29	97.31	0.072
ZTP2-112		97.25		
ZTP2-112		97.39		
ZTP2-114		97.28	97.32	0.047
ZTP2-114		97.37		
ZTP2-114		97.30		

 A uniform and reproducible batch of each of the four materials was produced and set aside for this testing. A small scale column sorption test was run to gather sorption and desorption data in a flow through scenario. This test yields the most significant insight into the sorption and desorption capability of the sorbent materials of interest. After the column testing the most effective materials were evaluated with additional testing to determine the maximum sorption capacity and to monitor sorption over time.

Small Scale Column Testing Results

A small- scale column sorption test was run with 4 chars and a sand control to gather sorption and desorption data in a flow through scenario. This test yields the most significant insight into the sorption and desorption capability of the sorbent materials of interest. After the column testing the most effective materials were further evaluated with additional testing to determine the maximum sorption capacity and to monitor sorption over time.

Test Procedure

A small hydrochar sample is mixed with sand to increase column bed volume for testing. The mixture is loaded into a plastic syringe, which serves as the column. A specific volume of solution containing radiolabeled pesticide is added to the loaded column and allowed to pass through gravimetrically. The solution which passes through the column is collected and analyzed for pesticide content. Then the amount of pesticide captured by the hydrochar can be calculated.

Table 6 illustrates the capacity of four stover materials to capture imidacloprid. Sand was used as an inert control to validate the test method. It was found that with this test method the raw corn stover and the stover treated only by HTC did not retain any imidacloprid after the "phase 2" rinsing steps as detailed in the procedure. Alternatively, the two materials which underwent PTT were able to each retain approximately 200ug imidacloprid per gram of material. This reinforces the importance of surface modification of the biomass or hydrochar to achieve sorption of the pesticide. It is also clear, that for a dry biomass source hydrothermal carbonization prior to PTT, is usually not necessary.

Table 6. Small Scale Colum Imidacloprid Sorption Test Results

Material Description	Phase 1 Imidacloprid Retained	Phase 2 Imidacloprid Released	Imidacloprid Retained after Phase 2	Imidacloprid Retained After Phase 2 (per gram material in column)
	(ug)	(ug)	(ug)	(ug/g)
Sand only (blank)	2.01	2.46	-0.45*	NA
Raw stover	7.50	8.24	-0.74*	NA
HTC only	4.17	4.44	-0.27*	NA
PTT only	52.2	1.45	50.7	204
HTC->PTT	50.1	4.78	45.3	182

*Note: A negative mass of imidacloprid retained is not possible, however a negative value was calculated due to a small bias in the measurement equipment. The retention was effectively zero.

The results are illustrated graphically in Figure 2 for sorption of pesticide and Figure 3 for column washing and potential desorption.

Figure 2. Column loading (Sorption)
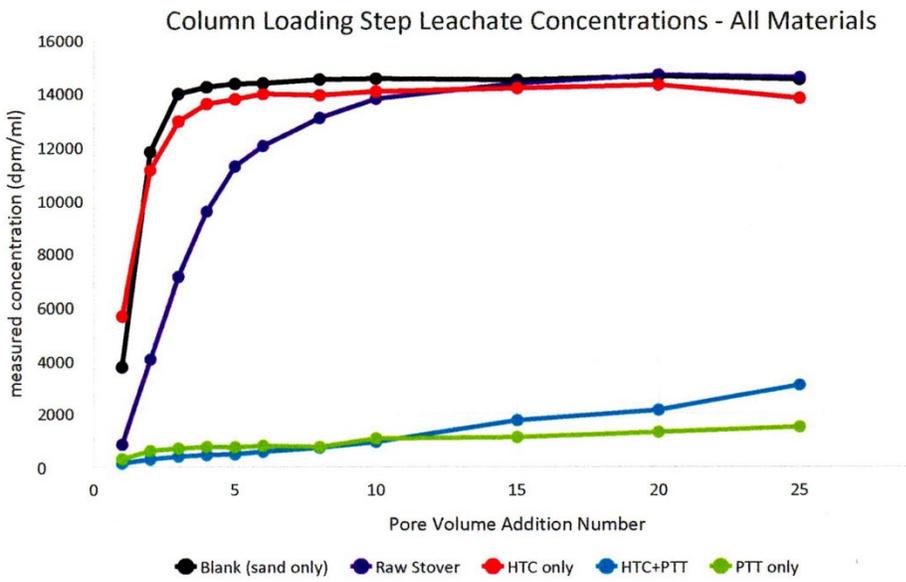
Figure 3. Column Washing (desorption)
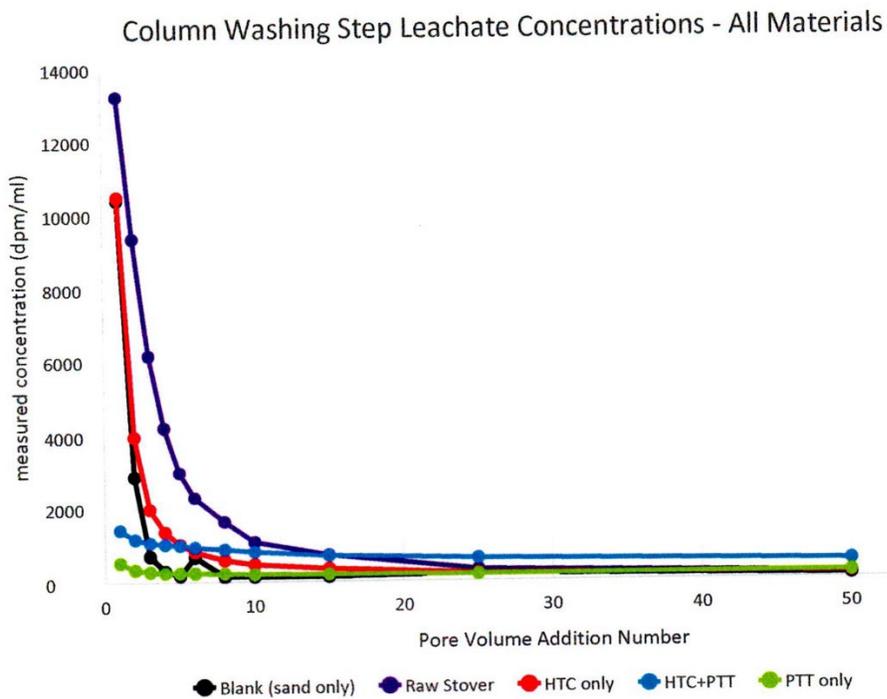
The test results for desorption, Figure 3, are problematic in that some "hot" pesticide was detected for the duration of the 25 cycles in the test. There are two possible explanations for this observed desorption.

1. The chars desorb some pesticide continuously
2. The chars are known to exhibit some attrition and in so doing could be carrying char with sorbed pesticide with the particulates flowing out of the column.

It is not clear if either one or both of these phenomena are being observed. Considerably more effort would have had to be expended to rationalize this issue and, while important, was well beyond the scope of this project. Large scale column testing would be necessary to determine if actual desorption is occurring. This requires experimentation at a considerably larger scale than bench testing in the laboratory which in turn entails equipment for making larger batches of char and larger post thermal treatment ovens as well as pelletizing equipment to compact the char in a form suitable for large column testing that will not be subject to attrition as water flows through the column or filter.

Follow up testing: time dependent removal
The two highest performing materials from the small column study underwent additional testing to observe the rate of imidacloprid removal over time. Each material was combined with a 1 ppm solution of imidacloprid in a vessel and placed on a linear shaker at 180 RPM. The amount of pesticide remaining in solution after certain time points was measured, see table 7.
Table 7: Percentage of imidacloprid removed from a challenge solution over time

Contact Time (hours)	SDP2-1	SDP2-2
0.5	88.5	96.0
1.0	90.4	96.7
2.0	96.1	84.2
3.0	97.1	97.9
5.0	96.7	97.8
7.0	97.6	97.8
24.0	97.9	97.9

The time dependent removal test showed that a 3- hour contact time is sufficient for each of these materials to remove imidacloprid from a 1ppm starting concentration solution. After this time the removal capacity appears to stabilize with approximately 98% removal which corresponds to a removal capacity of 98ug imidacloprid per gram material.

Maximum removal capacity determination and isotherm construction

Sorption isotherms for SDP2-1 (stover with HTC+PTT) and SDP2-2 (stover with PTT only). The raw data are tabulated in Tables 8 and 9 respectively and are illustrated in Figure 4.

Table 8: Performance of stover derived material for imidacloprid removal from water (SDP2-1) which has undergone HTC followed by PTT treatments

Imidacloprid Starting Concentration	Imidacloprid Final Concentration	Imidacloprid Removed
ug/ml	ug/ml	ug/g
0.1	0.00163	9.43
0.5	0.00743	48.4
1.0	0.03445	96.9
5.0	1.10608	388
10.0	3.35895	660

Table 9: Performance of stover derived material for imidacloprid removal from water (SDP2-2) which has undergone only PTT treatment

Imidacloprid Starting Concentration	Imidacloprid Final Concentration	Imidacloprid Removed
ug/ml	ug/ml	ug/g
0.1	0.00111	9.48
0.5	0.00648	49.1
1.0	0.02370	97.0
5.0	0.30350	471
10.0	1.59681	835

Figure 4 Sorption Isotherms for Imidicloprid

Imidacloprid Sorption Isotherms for SDP2-1 (HTC-PTT) and SDP2-2 (PTT only)

60

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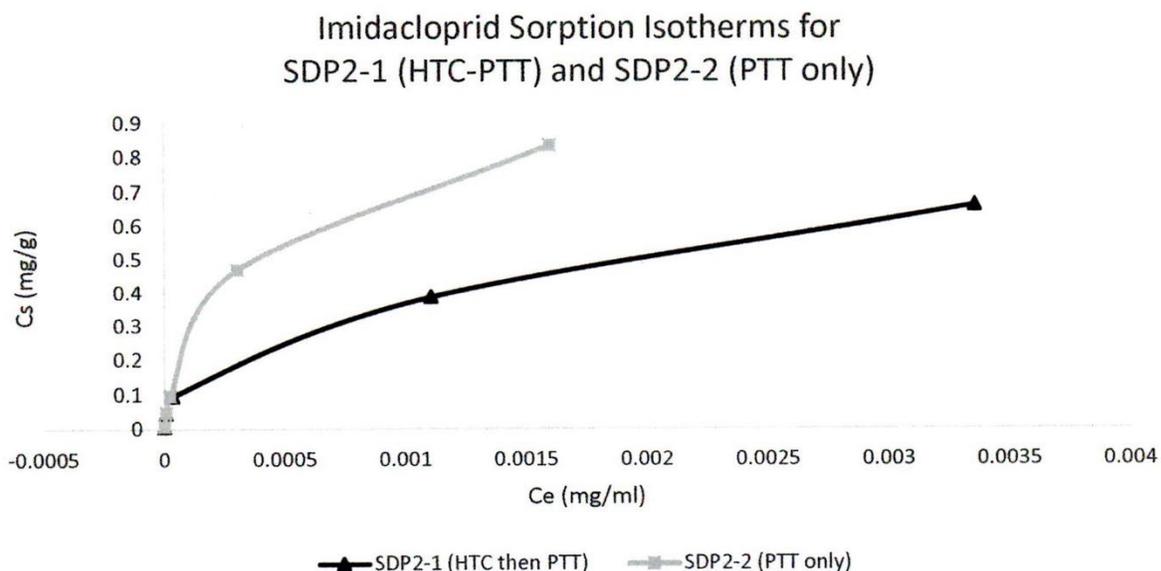
Incineration of Pesticide Loaded Char

Many studies over the years have demonstrated that incineration is an effective method for pesticide waste remediation. See Table 1 in "Incineration of Pesticides Wastes" by T. L. Ferguson and R. R. Wilkinson (Ref. 1) for a review of demonstrated remediation programs which achieved >99.99% destruction efficiency. Other reviews also conclude that incineration does achieve effective destruction and that combustion gases produced are similar to those from wood burning (Ref. 2). Additionally, the Minnesota Department of Agriculture has established incineration as preferred disposal method for waste pesticides (Ref. 3). Therefore, incineration is the recommended method for remediation of pesticide containing hydrochar filter materials.

References:
1. T. L. Ferguson and R. R. Wilkinson, "Incineration of Pesticide Wastes," Treatment and Disposal of Pesticide Wastes, ACS Symposium Series, Vol. 259, 1984, pp. 181-191.
2. A. S. Felsot, K. D. Racke and D. J. Hamilton, "Disposal and Degradation of Pesticide Waste," Reviews of Environmental Contamination and Toxicology, Vol. 177, 2003, pp. 123-200. doi:10.1007/0-387-21725-8_3
3. "Waste Pesticide Collection Program" MN Dept. of Agriculture https://www.mda.state.mn.us/chemicals/spills/wastepesticides.aspx

Conclusions for Pesticides

Many agricultural residues were evaluated for their ability to remove pesticides from solution. The residues were either converted to hydrochar or biochar and tested for various chemical classes. What did we find?

- Testing was focused on herbicides and insecticides utilized heavily in Minnesota
- Primary focus was on glyphosate herbicide and Imidacloprid, a neonicotinoid insecticide
- Neither hydrochars nor corn stover showed any capacity for removal of pesticides.
- When these same hydrochars were subjected to PTT (post thermal treatment) at 600 ^{0}C in an inert atmosphere to modify the structure, they showed a capacity for removal of pesticides.
- It is not clear if PTT increases surface area or modifies surface chemistry of the hydrochars or both.
- Dry biomass, like cornstover, can be converted directly to a biochar by PTT that will remove pesticides.
- Wet biomass like manures must first be converted by HTC to hydrochar and then PTT. Because wet manures are very problematic to process without converted them to a solid, drying would be too expensive because of the high water content >90%
- In small column tests some desorption was detected. Exact cause is not clear and would require significantly more testing in large columns to discern.

Outcomes 1,2 and 3 were completed.

Outcome 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*).

There were no desorption isotherms modeled since the desorption testing also demonstrated continual uptake of the pesticide. These observations suggest that the 1-week period was insufficient for equilibrium for all the sorption sites to be occupied. Additionally, we could not hold the pesticide sorption isotherms longer, due to the complication from pesticide degradation (abiotic pathways). This prohibited the determination of the desorption isotherms in this study.

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:
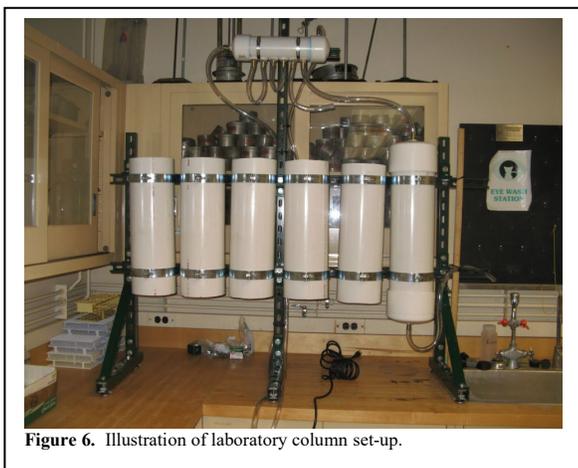
Figure 6. Illustration of laboratory column set-up.

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, 2017)

ENRTF Budget:	$ 47,180
Amount Spent:	$ 47,180
Balance:	$ 0

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, 2018

Activity Status as of *[July 30,2017]***:**

 Small lab scale column tests have been initiated with pesticides. Large scale tests may be both unnecessary and impractical. The latter because of the relatively small amounts of hydrochar that can be produced in a reasonable time period with the existing lab scale reactors.

Activity Status as of *[Dec. 31, 2017]***:**

Column testing

As indicated in the last activity status (July, 30, 2017), column testing is feasible only at lab scale because of scale limitations in our char production capacity. As indicated in the current status section for Activity 4, column testing for pesticide sorption will be conducted in a column wherein a pulse of radio-labelled Imidacloprid pesticide is injected in a small gravimetric flow column and the amount of pesticide captured is determined by count and subsequent calculation. For radio-labelled pesticides that are very expensive, this gives the most accurate and scalable results concerning the kinetics of pesticide sorption.

Phosphorous sorption column testing will be with a small flow column that will be utilized to measure phosphorous breakthrough to assess sorption kinetics for selected modified chars. A Hach spectrophotometer will be used to determine when phosphorous breakthrough occurs. From these data, kinetic curves can be constructed.

Final Report Summary: July 30, 2018

As discussed previously, a flow-through column study for hydrochar capacity for removal of phosphorus, pesticides and nitrates from water is not feasible for several reasons:

- *With our existing lab scale Paar reactors only small quantities of hydrochar can be produced in a reasonable time period.*
- *For pesticide testing an inert gas furnace, considerably larger than ours, would be required to convert hydrochar to bio-hydrochar.*
- *A flow-through column test would require that the char material, which is a fine granulation, be pelletized to avoid attrition and elution from the column. Pelletizing equipment is not available on the Twin Cities campus.*
- *Developing a useable pellet is in itself a significant research project to evaluate binders, pellet geometry, die design and the like.*
- *The information to be gained from "laboratory" column testing does need to be at a large scale. Kinetic data for phosphorus removal from small scale column tests are just as valid and useful as larger scale tests since the geometry of the columns permits accurate scale-up calculations.*

- *Large scale flow-through column work for pesticide removal is problematic and expensive because of the use of radio-labelled pesticides which are necessary to get accurate data at the low concentrations typical of pesticide loading in agricultural waters. The design for safe-handling of radio-labelled material in a large column is not straight forward and is beyond the scope of this project.*

Small column testing for pesticides was conducted in a column wherein a pulse of radio-labelled Imidacloprid pesticide was injected in a small gravimetric flow column and the amount of pesticide captured was determined by count and subsequent calculation. For radio-labelled pesticides that are very expensive, this gives the most accurate and scalable results concerning the kinetics of pesticide sorption. Results of these tests are detailed in the Activity 4 final report section.

Phosphorus removal from water testing was achieved with a small flow column utilized to measure phosphorous breakthrough to assess sorption kinetics for selected modified chars. A Hach spectrophotometer was used to determine when phosphorous breakthrough occured. From these data, kinetic curves were constructed. These could be utilized to design a larger column for field trials. Detailed data are provided in the Activity 3 Final Report section.

Future Work

Proof of principle for phosphorus removal from water has been established by this project The next logical step to advance the technology is a field trial---a fast-paced project establishing efficacy and measuring phosphorus removal under field conditions. This requires equipment on a larger scale to make sufficient quantities of modified chars. The needed equipment is available within the University at the NRRI (Natural Resources Research Institute) in Duluth. The field trial would encompass several activities;

• Fabricating phosphorus removing, metal-char pellets made from agricultural residues

• Fabricating pellets and coating with polymers to enhance retention of phosphorus, as needed.

• Constructing and testing a prototype drain tile filter for phosphorus removal at pilot scale and   in field trials.

• Evaluate metal and phosphorus recovery from phosphorous saturated pellets.

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, 2017)　　　　　**ENRTF Budget:**　**$ 60,871**

　　　　　　　　　　　　　　　　　　　　　　　　　　　Amount Spent:　**$ 60,871**

　　　　　　　　　　　　　　　　　　　　　　　　　　　　　　　Balance:　**$ 0**

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, 2017
2. Examine the potential toxicity of modified hydrochars to aquatic macro invertebrates.	Dec.31, 2017
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 30,2018

Activity Status as of *(July30, 2017)*
Hydrochars produced with lanthanum as the activating metal have emerged as the most effective with respect to phosphate removal from water. Therefore, our primary concern for possible hydrochar toxicity is related to the lanthanum metal which is present on the hydrochar. A literature review is underway to assess the toxicity of lanthanum in the environment, with a particular focus on potential effects toward aquatic life. Laboratory experiments are being planned to assess toxicity toward aquatic life by monitoring the impact of a lanthanum hydrochar on daphnia.

Activity Status as of *[Dec.31, 2017]*:

Toxicity Screening of Lanthanum Modified Hydrochars

The purpose of the toxicity screening conducted in this study was to assess if the hydrochar was acutely toxic to water life (assessed through *Daphnia* toxicity screening), and if lanthanum modified hydrochars (in-situ and post addition) were toxic to the *Daphnia* organisms.

The method used was based on the US EPA Method 2021 (US EPA, 2001) with the main deviation being the laboratory culturing of the organisms. The D. magma was used immediately upon receipt from the supplier. The package was opened, and the organisms were initially inspected for activity.

　　　The *D. magna* test has typically been demonstrated to be a more sensitive indicator of toxicity than bioassays using more complex organisms (e.g., Guilhermino et al., 2000). This then was a conservative assessment of the potential toxicity of the hydrochar products. The test results after 24 hours are shown in Fig. 1 for the control, char alone, char with lanthanum added in-situ and char with post added lanthanum.
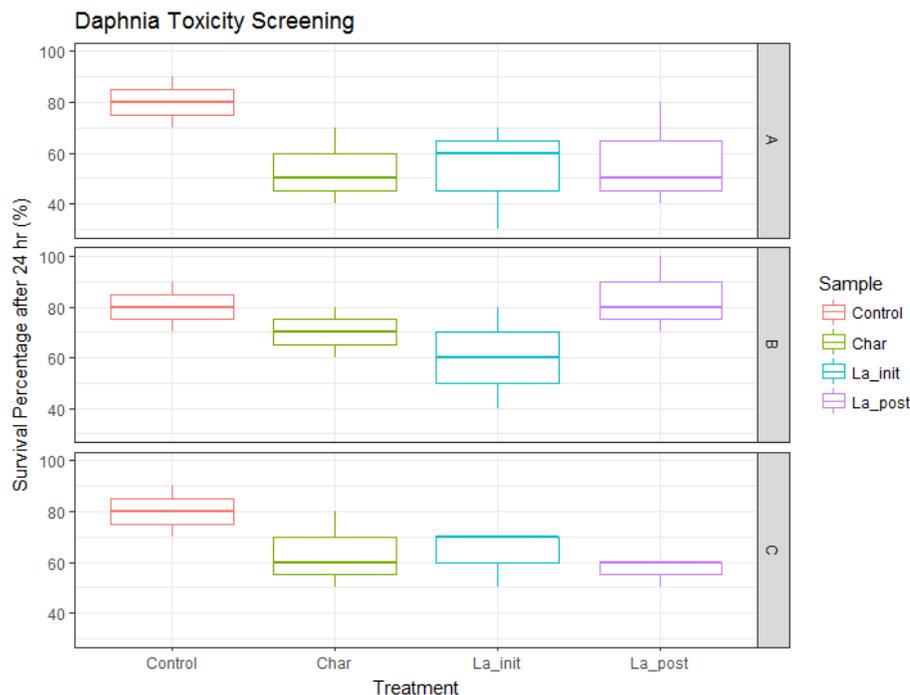
Figure 1. The results of the toxicity screening for the hydrochar (Char), lanthanum in-situ (La_init), and post-addition lanthanum (La_post) products compared to the control (Control)

The control set was slightly lower than the recommended mortality given in guidelines on the acute *D. magna* assays, where the percentage mortality (or immobilization) in the controls should be ≤ 10% at the end of the exposure time (OECD, 2004). In our experiments, this was slightly higher at 20% mortality in the control replicates (80% survival). We hypothesize that this criterion was not meet due to the fact that the *Daphnia magna* were purchased from a supplier (Carolina Scientific Supply) and used upon receipt, and not cultured in the laboratory. This was the major contributing cause of this lower than recommended survival rate.

Conclusions

The data suggest that the toxicity of the hydrochar is primarily due to the hydrothermal carbonization step, and not from the lanthanum addition itself. There are numerous potential organic acids and low weight molecular compounds that are produced during the hydrothermal carbonization treatment, but the exact chemical toxin is unknown.
 This would be supported by the lower numerical results in the post-La addition, since this hydrochar would be rinsed again during this post-lanthanum addition and thus reduce the concentration of potential toxins emanating from the char itself. However, since this was not fully examined in this work, this still requires further research to elucidate the exact reason for the toxicity observed. This would require testing with chars receiving increasing rinse cycles and monitoring the subsequent daphnia toxicity.

References

Guilhermino, L., Diamantino, T., Silva, M.C., Soares, A.M., 2000. Acute toxicity test with *Daphnia magna*: an alternative to mammals in the prescreening of chemical toxicity? *Ecotoxicol Environ Saf.* 46(3):357-62.

Final Report Summary: July 30, 2018

Outcome 1**.** *Ca***lculate 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.**

This is not feasible without large scale or field trials to obtain meaningful data with which perform the design calculations. This was discussed in the Final Report for Activity 5. It also was recommended that a field trial be conducted as the next step to achieve implementation on a wide scale.

Outcome 2. **Examine the potential toxicity of modified hydrochars to aquatic macro invertebrates.**

As stated in the activity status update of Dec 31,2017**,** The purpose of the toxicity screening condu was to assess if the hydrochar was acutely toxic to water life (assessed through *Daphnia* toxicity screening), and if lanthanum modified hydrochars (in-situ and post addition) were toxic to the *Daphnia* organisms. The details are given in the Dec31, 2017 update.

To summarize, the data suggest that the toxicity of the hydrochar is primarily due to the hydrothermal carbonization step, and not from the lanthanum addition itself. There are numerous potential organic acids and low weight molecular compounds that are produced during the hydrothermal carbonization treatment, but the exact chemical toxin is unknown. This would be supported by the lower numerical results in the post-La addition, since this hydrochar would be rinsed again during this post-lanthanum addition and thus reduce the concentration of potential toxins emanating from the char itself. This also implies that more thorough rinsing of the hydrochar to remove more of the organics of the interstitial liquid held loosely by the char would reduce the toxicity. Since the recommended method for lanthanum incorporation is by post addition it is important to note that the lanthanum attached to the char in this manner was not found to be toxic. More thorough rinsing of the char prior to lanthanum addition should prove beneficial.

Outcome 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.**

With hindsight, it is recognized that a handbook describing how to use modified hydrochars to improve the aquatic ecosystem cannot be written without field trial data. As indicated in the final report section for activity 5, there are several reasons why that is beyond the scope of this project. Field trials are the next logical step to move this technology from the laboratory to land managers and farmers. What had been accomplished in this project is "proof of principle"

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, 2017]***:**

The Office for Technology Commercialization of the University of Minnesota has **committed to a provisional patent filing** on the simultaneous sorption of phosphate and glyphosate (a herbicide that contains phosphorous) by a lanthanum modified hydrochar.

Status as of Dec.31, 2017

Glyphosate
The university filed a provisional patent entitled, METHOD FOR REMOVING AN ORGANOPHOSPHOROUS COMPOUND FROM AN AQUEOUS MEDIUM, on Dec. 11, 2017.

Final Report Summary: July 31, 2018

The University has expanded the scope of the original provisional patent to include broader claims. The new provisional patent is: U.S. Provisional Application No. 62/718,705
Title: METHOD FOR REMOVING PHOSPHORUS COMPOUNDS FROM AN AQUEOUS MEDIUM, on August 14,2018

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

IX. VISUAL COMPONENT or MAP(S):

PREVENTING PHOSPHOROUS AND PESTICIDES FROM ENTERING WATER RESOURCES THROUGH DRAINTILES
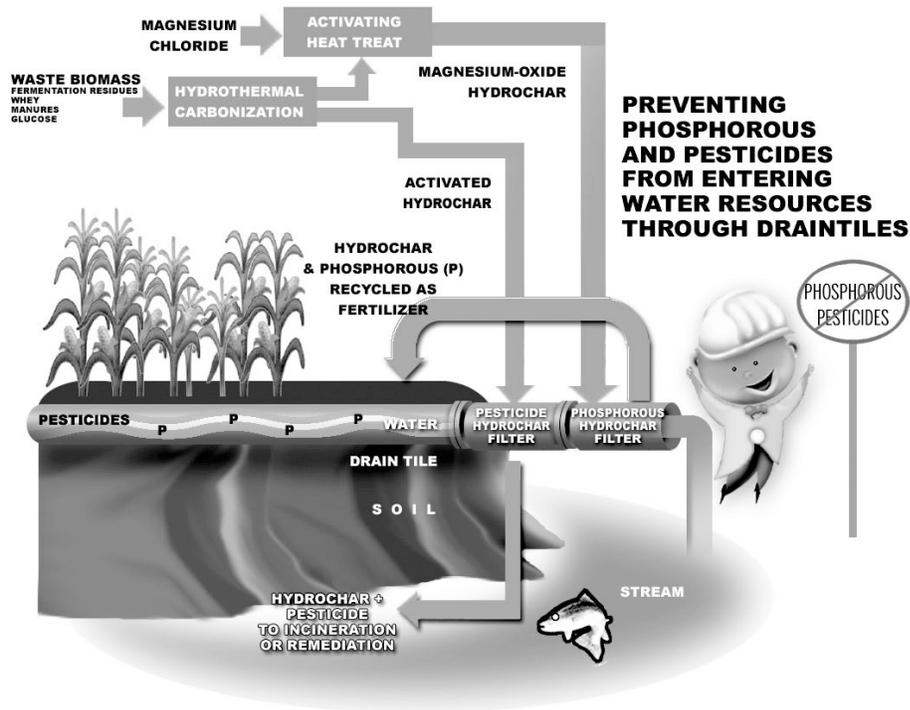
X. RESEARCH ADDENDUM: Submitted as separate document.

XI. REPORTING REQUIREMENTS:

Periodic work plan status update reports will be submitted no later than *(Dec. 31, 2015*], [*July 30, 2016*], (Dec. 31, 2016, (July 30, 2017) and [*Dec. 31, 2017*]. A final report and associated products will be submitted between June 30 and August 15, 2018.

Environment and Natural Resources Trust Fund
M.L. 2015 Project Budget Final Attachment A

Project Title: Preventing Phosphorous and Pesticides from Entering Water Resources Through Draintiles
Legal Citation: M.L. 2015, Chp. 76, Sec. 2, Subd. 04d
Project Manager: Kenneth J. Valentas
Organization: University of Minnesota
M.L. 2015 ENRTF Appropriation: $ 505,000-
Project Length and Completion Date: 3 years , June 30, 2018
Date of Report: 8/17/2018

ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Activity 1 Budget	Amount Spent	Activity 1 Balance	Activity 2 Budget	Amount Spent	Activity 2 Balance	Revised Activity 3 Budget 7/24/18	Amount Spent	Activity 3 Balance	Reised Activity 4 Budget 7/24/18	Amount Spent	Activity 4 Balance	Revied Activity 5 Budget 7/24/18	Amount Spent	Activity 5 Balance	Revised Activity 6 Budget 7/24/18	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	$0	$34,633	$34,633	$0	$41,214	$41,214	$0	$116,149	$116,149	$0	$44,435	$44,435	$0	$58,871	$58,871	$0	$423,433	$0
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 years = 1FTE			$0			$0			$0			$0			$0			$0		$0
TBD Biotechnology Institute Research Associate, Conduct and supervise hydrothermal carbonization/hydrochar experiments, $76,267 (92.5% salary, 7.5% fringe), 0.4FTE for 1.5 years = 0.6FTE			$0			$0			$0			$0			$0			$0		$0
Research technician,TBN, $49,100 (78.6% salary, 21.4% fringe)100% for one year = 1.0FTE			$0			$0			$0			$0			$0			$0		$0
Grad. Student, EEB Dept. TBN, $44,500, (52.1 % salary, 47.6% fringe), 100% for I year = 1 FTE			$0			$0			$0			$0			$0			$0		$0
Grad student(PhD),, TBN, Soils Dept. $40325 (55.3% salary, 47.9% fringe), 50% for 2 years = 1FTE.			$0			$0			$0			$0			$0			$0		$0
Grad student (MS), TBN,Soils Dept., $33824, (49.5%salary, 50.5% fringe), 37.5% for two years = 0.75 FTE			$0			$0			$0			$0			$0			$0		$0
Undergraduate student workers; 25 hrs./week x104 weeks = 1.25FTE ; 2600 hrs. @ $13.22/hr $34372. (no fringe)			$0			$0			$0			$0			$0			$0		$0
Professional/Technical/Service Contracts			$0			$0			$0			$0			$0			$0		$0
Handbook preparation (graphics and typing)			$0			$0			$0			$0			$0			$0		$0
Equipment/Tools/Supplies			$0			$0			$0			$0			$0	$2,000	$2,000	$0	$2,000	$0
Analysis and testing for phosphorous, nitrates, carbon content, surface area(SEM),			$0			$0			$0			$0			$0			$0		$0
Char Fac user fees $50/hr. x 300 hrs.	$16,519	$16,519	$0	$780	$780	$0			$0			$0			$0			$0	$17,299	$0
Probes for nitrate, dissolved oxygen, pH			$0	$10,000	$10,000	$0	$46	$46	$0			$0			$0			$0	$10,046	$0
PVC Fittings and tubing for flow through column and calibration standards			$0	$2,632	$2,632	$0	$477	$477	$0			$0			$0			$0	$3,109	$0
Consumable supplies			$0			$0			$0			$0	$2,745	$2,745	$0			$0	$2,745	$0
Pesticide standards, centrifuge tubes	$2,250	$2,250	$0	$330	$330	$0	$130	$130	$0	$1,395	$1,395	$0			$0			$0	$4,105	$0
Radio labelled pesticides			$0			$0			$0	$7,050	$7,050	$0			$0			$0	$7,050	$0
GC analytical column			$0			$0			$0	$5,700	$5,700	$0			$0			$0	$5,700	$0
LC-Mass Spec 100 samples x $120			$0			$0			$0	$0	$0	$0			$0			$0	$0	$0
Toxicity testing			$0			$0			$0	$500	$500	$0			$0			$0	$500	$0
Pump for flow through column			$0			$0			$0			$0			$0			$0	$0	$0
Capital Expenditures Over $5,000			$0			$0			$0			$0			$0			$0	$0	$0
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 $3,500.Total =$32,600			$0			$0			$0	$28,923	$28,923	$0			$0			$0	$28,923	$0
Printing of users handbook			$0			$0			$0			$0			$0			$0	$0	$0
Open access publication for public dissemination of technical research results			$0			$0			$0			$0			$0			$0	$0	$0
Travel expenses in Minnesota			$0			$0			$0			$0			$0			$0	$0	$0
in state travel to secure soil sample, aquatic samples and the like. Anticipated mileage charges of $400.			$0			$0			$0	$90	$90	$0			$0			$0	$90	$0
COLUMN TOTAL	$146,900	$146,900	$0	$48,375	$48,375	$0	$41,867	$41,867	$0	$159,807	$159,807	$0	$47,180	$47,180	$0	$60,871	$60,871	$0	$505,000	$0