

Metropolitan Water Reclamation District of Greater Chicago

> Welcome to the June Edition of the 2021 M&R Seminar Series

NOTES FOR SEMINAR ATTENDEES

- All attendees' audio lines have been muted to minimize background noise.
- A question and answer session will follow the presentation.
- Please use the "Chat" feature to ask a question via text to "All Panelists".
- The presentation slides will be posted on the MWRD website after the seminar.
- This seminar has been approved from the ISPE for one PDH, and pending approval from the IEPA for one TCH. Certificates will only be issued to participants who attend the entire presentation.

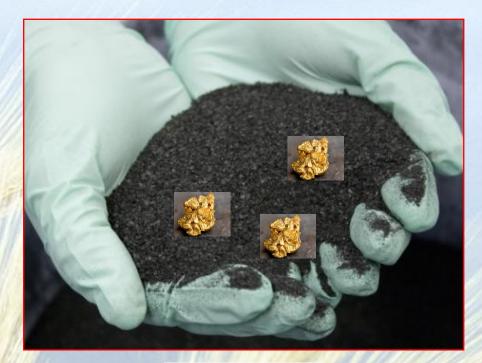
Principal Research Scientist Illinois Sustainable Technology Center/Prairie Research Institute University of Illinois at Urbana-Champaign

Wei Zheng, Ph.D.



Dr. Wei Zheng is a principal research scientist at the Illinois Sustainable Technology Center (ISTC)/Prairie Research Institute (PRI) at the University of Illinois at Urbana-Champaign (UIUC). He is also an adjunct faculty member at UIUC. He joined the ISTC/PRI/UIUC in 2008. Prior to joining the ISTC, he worked as a post-doc and soil scientist at USDA-ARS, Salinity Laboratory and University of California, Riverside. He earned a Ph.D. in Environmental Chemistry from Zhejiang University (China). He has expertise in environmental science and environmental chemistry with extensive experience on the fate and transport of pesticides and emerging contaminants including pharmaceuticals and personal care products (PPCPs) and per- and polyfluoroalkyl substances (PFAS), remediation techniques for chemical pollutants, and production and utilization of biochar. Currently, he has multiple on-going projects funded from USDA, USEPA, DOE and IL NREC, which are related to biochar.

Biochar in Soil and Environmental Applications



Wei Zheng

Illinois Sustainable Technology Center University of Illinois at Urbana-Champaign <u>weizheng@illinois.edu</u>

Metropolitan Water Reclamation District of Greater Chicago (MWRDGC)

June 25, 2021

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Illinois Sustainable Technology Center (ISTC)

The Illinois Sustainable Technology Center (ISTC) is a Division of the Prairie Research Institute (PRI) at the University of Illinois (U of I). ISTC (formerly Illinois Waste Management Research Center) has been providing research, scientific expertise, and data that benefit the environment, economy, and people of Illinois and beyond. It used to be Illinois State Agency.

Current ISTC missions include:

- > Research
- Technical assistance
- Technique demonstration
- Communication

http://www.istc.illinois.edu/



Acknowledgments

Sarmila Katuwal > Nathan Pflugmacher Marisa Moreno > Mahelet Maru Siming Yang > John Scott ≻ Wiles, K. > Murali, D. ➢ Manandhar, J >Joe Pickowitz ≻Dr. Sharma, B.K. >Dr. Richard Cooke **Dr. Rajagop**anlan, K.

Illinois Agriculture

MWRD

- Dr. Olawale Oladeji
 Dr. Guanlong Tian
 Dr. Albert Cox
 Jacob Baylor
 Dr. Edward Podczerwinski
- ≻Dr. Dominic Brose

Lauren Lurkins
 Elaine Stone
 Dr. Lakhwinder Hundal





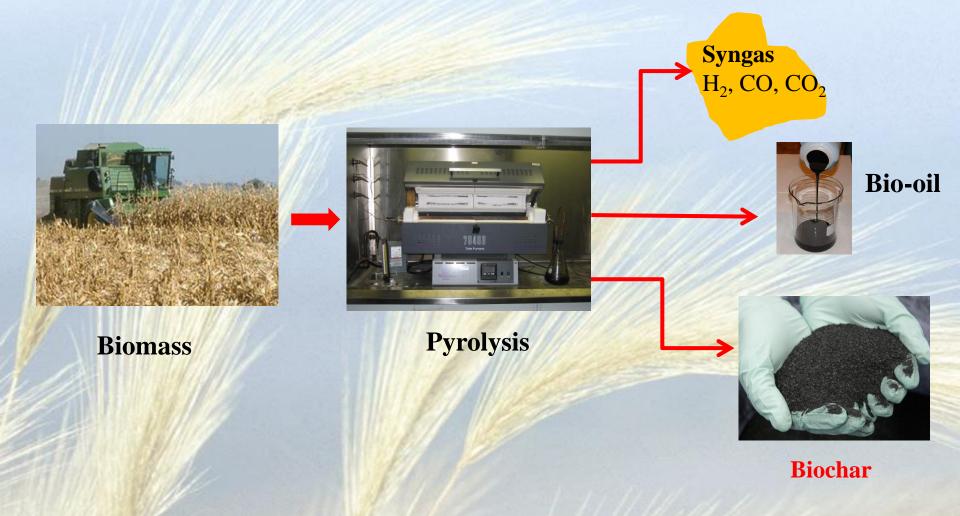
<u>U of I Academic Professional Development Fund (APDF)</u> <u>Illinois H</u> & Russell and Helen Dilworth Memorial Fund

Illinois Hazardous Waste Funds



What is Biochar?

Biochar is a carbon-enriched material produced from biomass under a limited supply of oxygen. "Not a high-tech product".



Biochar vs Other Carbons

- Biochar is similar in its appearance to charcoal, char, activated carbon, and other black carbon materials. While biochar is produced from waste biomass, it can provide the following benefits.
 - ***** Waste reduction
 - Energy production
 - Contaminant sorbent
- The difference of biochar and carbon-rich materials: Biochar is produced from biomass with the intent to deliberately apply to soil for:
 - Soil Amendment
 - * <u>Carbon Sequestration</u>





Biochar Applications in Soil and Environment

Overall, biochar applications in soil and environment can provide multiple valuable benefits, such as E³ (Energy, Environmental, Economic) profits.

Our biochar studies focus on:

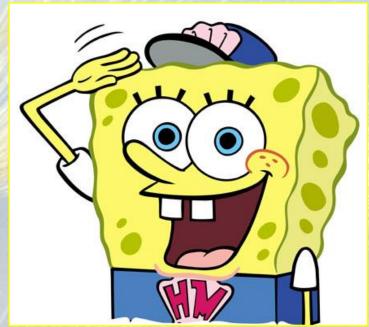
- Soil amendment
- Carbon sequestration
- Environmental Applications
 - Nutrient capture
 - Emerging contaminant removal



Biochar as a Soil Amendment

Once biochars are added to soil, they can **boost soil fertility and improve soil quality** by

- trapping moisture
- helping the soil hold nutrients
- attracting more beneficial fungi and microbes
- improving cation exchange capacity
 (CEC)
- raising soil pH
- others....



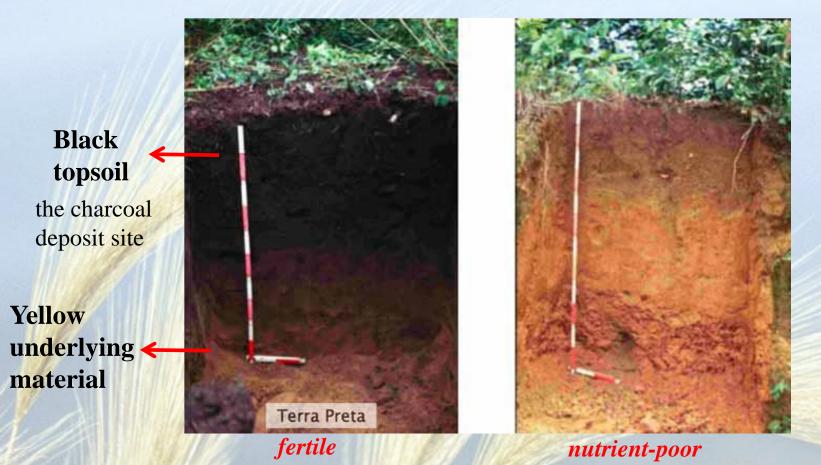
Biochar & Slash-and-Burn

- Slash-and-burn is a specific functional element of certain farming practices, often shifting cultivation systems. Before artificial fertilizers were available, it was traditional fertilization method. Burning removes the vegetation and may release a pulse of nutrients to fertilize the soil.
- Slash-and-char is an alternative to slash-and-burn that has a lesser effect on the environment. Switching from "slash-and-burn" to "slash-and-char" can prevent the rapid deforestation and subsequent degradation of soils. It results in the creation of biochar, which can

then be mixed with biomass such as crop residues, food waste, manure or other, and buried in the soil to bring about the formation of terra preta. Terra preta is one of the richest soils n on the planet.



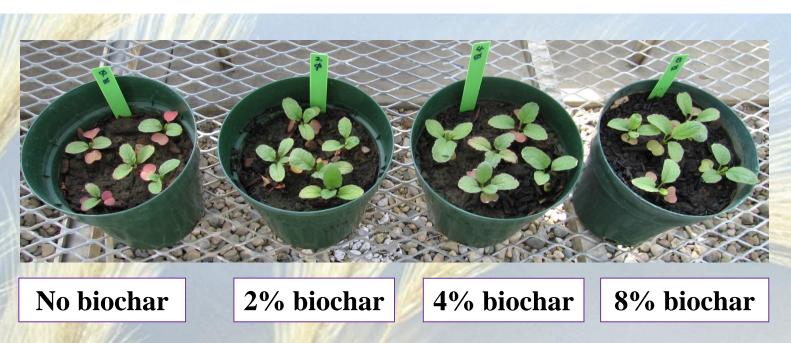
Amazonian Dark Soil---terra preta



Comparison of profiles of *terra preta* and adjacent soils ----From: IBI website

Biochar as a Soil Amendment

- However, biochar additions to soils have not consistently resulted in increased crop yields. It has been reported that approximately 50% of the studies showed shortterm yield increases after biochar soil application, 30% observed no significant differences, and 20% noted negative yield or growth impact.
- Another burrier for biochar large scale application is cost --- improving biochar values to cover the cost.



Projects on Biochar & Chemical Fertilizer Reduction

This study is to investigate if the use of biochar as a soil amendment in **Illinois rich soils** can reduce chemical fertilizer use while at the same time maintaining or increasing crop yields. To achieve this goal, three tasks were undertaken in the project:

Biochar production and characterization:

Biochar production through a low-temperature slow pyrolysis technique from a variety of waste biomass.

Sorption of nutrients by biochar:

The sorption kinetics and mechanisms of NH_4^+ and PO_4^{3-} removal by biochar were investigated.

Greenhouse and Field trial:

Demonstrate the efficacy of biochar as a simple soil amendment as measured by crop yields and lowered fertilizer use in Illinois rich soils.

Illinois Hazardous Waste Funds & <u>Russell and</u> <u>Helen Dilworth Memorial Fund</u>



Biochar Application in Greenhouse

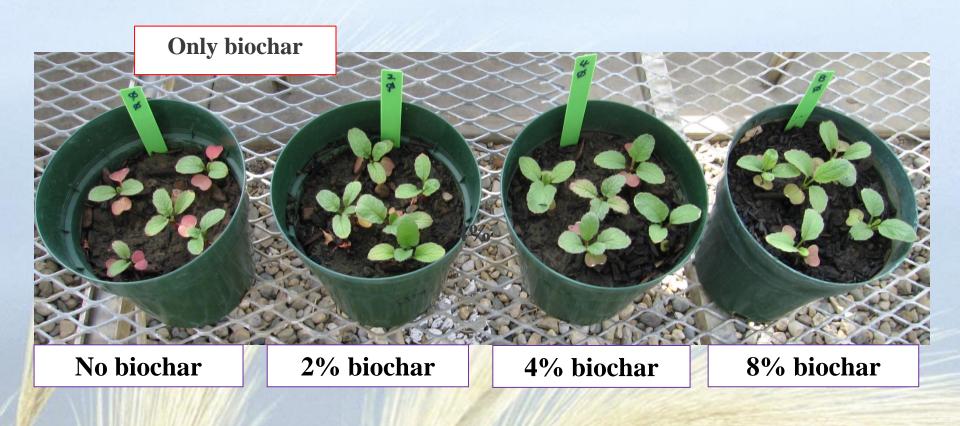
We used a radish as a target plant to evaluate the effect of different application rates of biochars and nitrogen fertilizers on crop yields.

- Biochar application rates: 0, 2%, 4%, 8% (w/w).
- Nitrogen fertilize (NH₄NO₃) rates: 0, 25, 50, and 100 lbs N/acre.



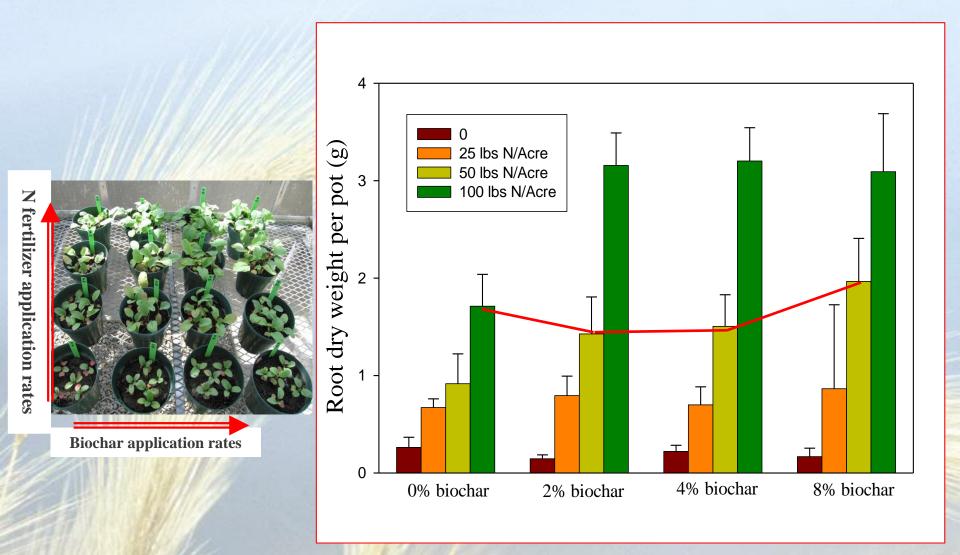


Biochar Application in Greenhouse



In the absence of fertilizer, biochar use resulted in no improvement in either radish plant growth or crop yields.

Biochar Application in Greenhouse



Biochar Application in Illinois Corn Fields

Biochar Research Plot

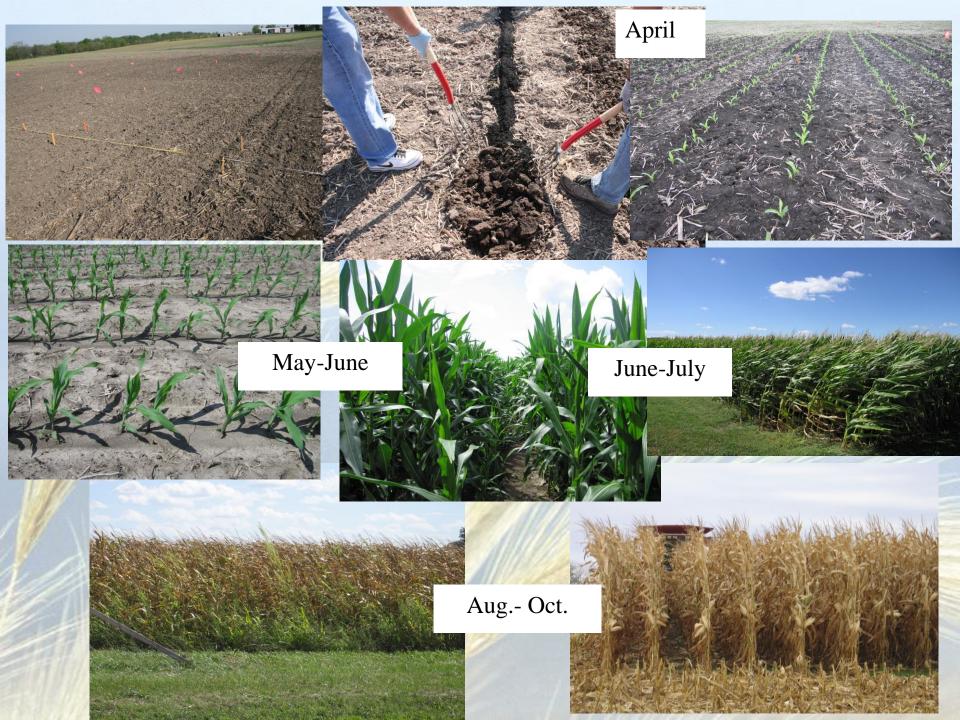


Illinois Sustainable Technology Center

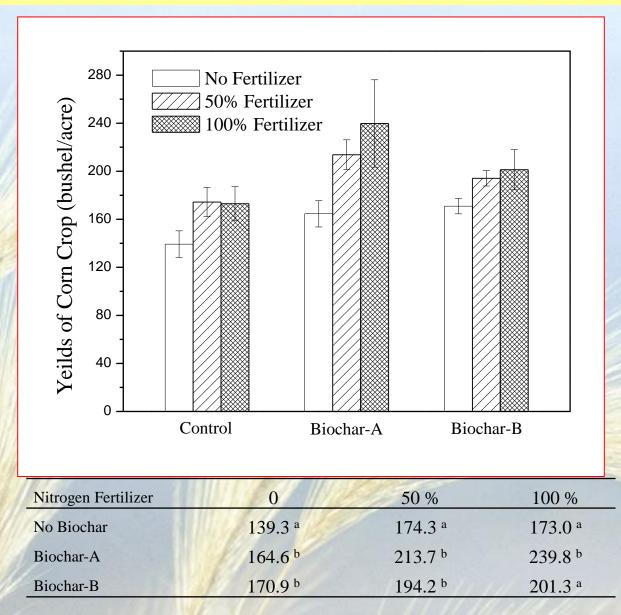
HALLAND CALLA STANDING

University of Illinois at Urbana-Champaign

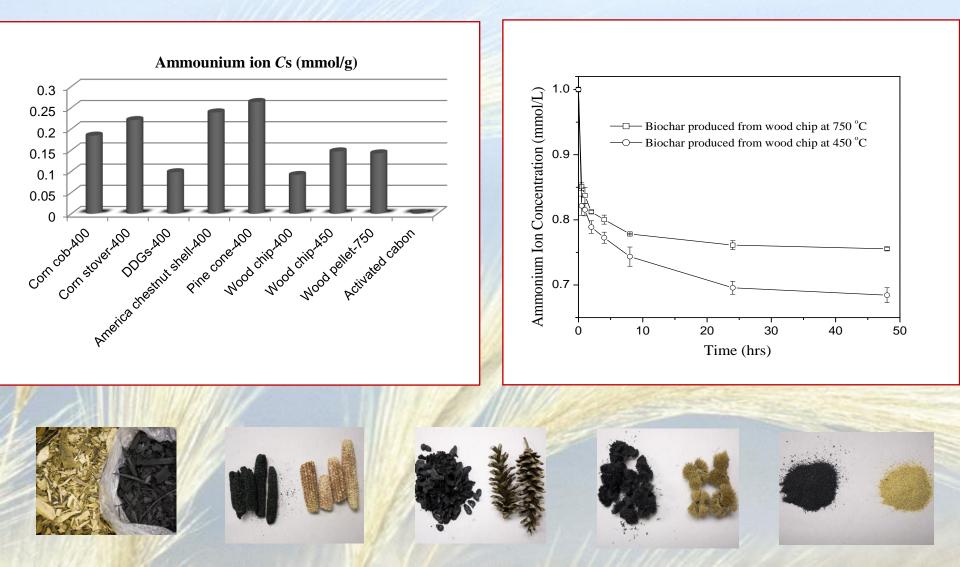
Sponsored by: Illinois Department of Agriculture Sustainable Agriculture Grant Program



Biochar Application in Corn Field



Sorption of NH₄⁺ on Various ISTC's Biochars



Biochar Applications in Soil and Environment

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- Soil amendment
- Carbon sequestration
- Environmental Applications
 - Nutrient capture
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Global Climate Change and Global Warming



Positive proof of global warming.

Global Climate change is a big challenge

Large emissions of greenhouse gases, primarily from CO₂

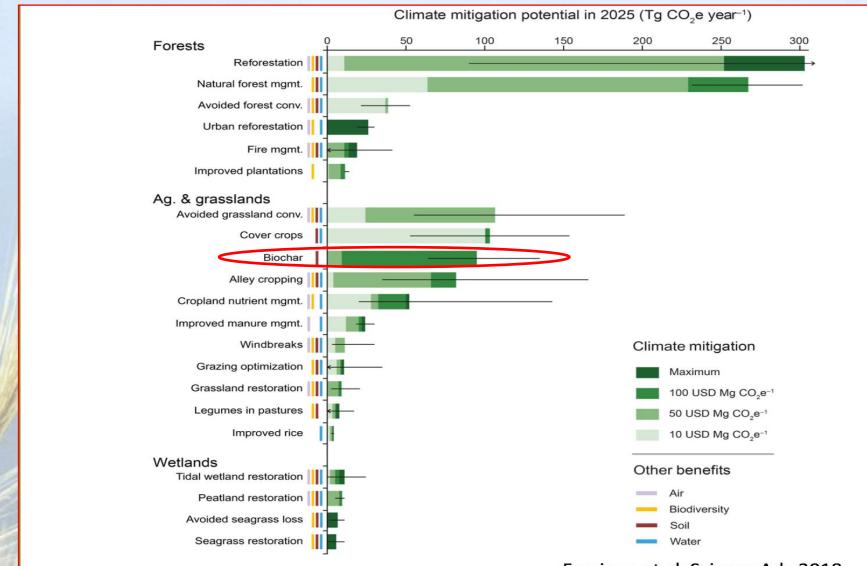


Global atmospheric concentration of CO₂

Global atmospheric concentration of CO₂ (since industrial revolution)

Arendal

Climate mitigation from "nature-based" activities



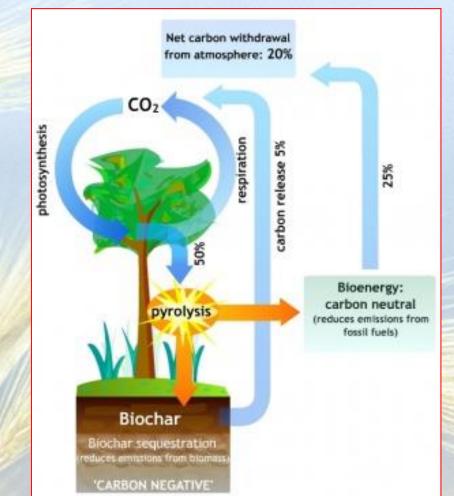
Fargione et al, Science Adv 2018

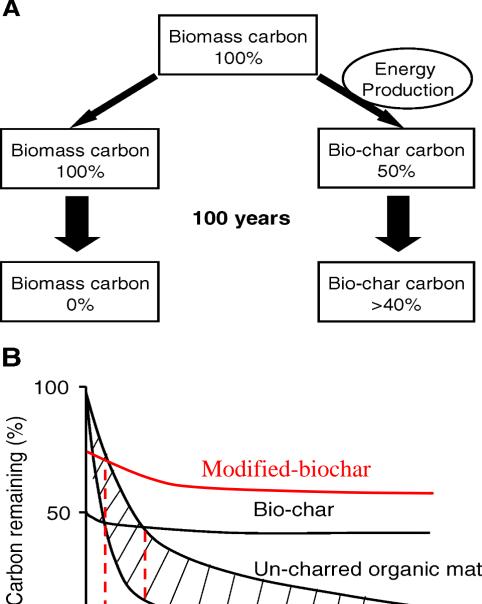
How does Biochar Sequester Atmospheric Carbon?

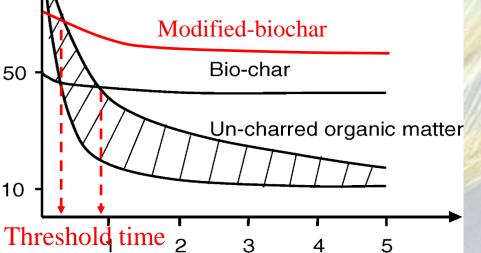
Biochar is one of feasible solutions to reduce the growing levels of CO_2 in the atmosphere.

The natural carbon cycle is carbon neutral. If we use pyrolysis to produce biochar from waste biomass, we can lock up 50% biomass carbon into biochar. Considering carbon in biochar can stores in soils for a long term, the net process is carbon negative. Therefore, biochar production from biomass and its application into soils has a great potential to alleviate climate change.









Years

Carbon Footprint Analysis

Schematics for biomass or biochar remaining after charring and decomposition in soil.

(A) C remaining from biomass decomposition after 100 years from IPCC; C remaining after charring or pyrolysis; bio-char C remaining after decomposition. (B) range of biomass C remaining after decomposition of crop residues and estimation of bio-char.

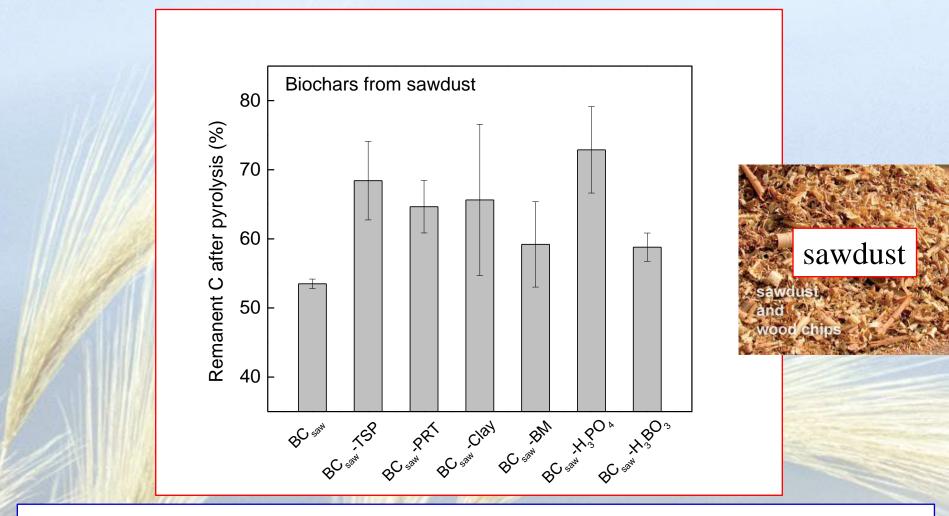
From: Lehmann et al. 2006 in Mitigation and Adaptation Strategies for Global Change

Projects on Improving Biochar Carbon Sequestration Capacity

- The technique is to pre-treat biomass by mixing some passivator-like materials to retain more biomass carbon in biochar during pyrolysis.
- The objective of this research project is to use chemical modification methods to strengthen carbon retention and stability in biochar.

This study is being supported by **Russell and Helen Dilworth Memorial Fund**

Effect of Chemical Additives on Carbon Retention



Six P-rich chemicals or passivator-like materials were chosen as chemical additives in this study: triple superphosphate (TSP), phosphate rock tailing (PRT), bonemeal (BM), clay, H₃PO₄, and H₃BO₃.

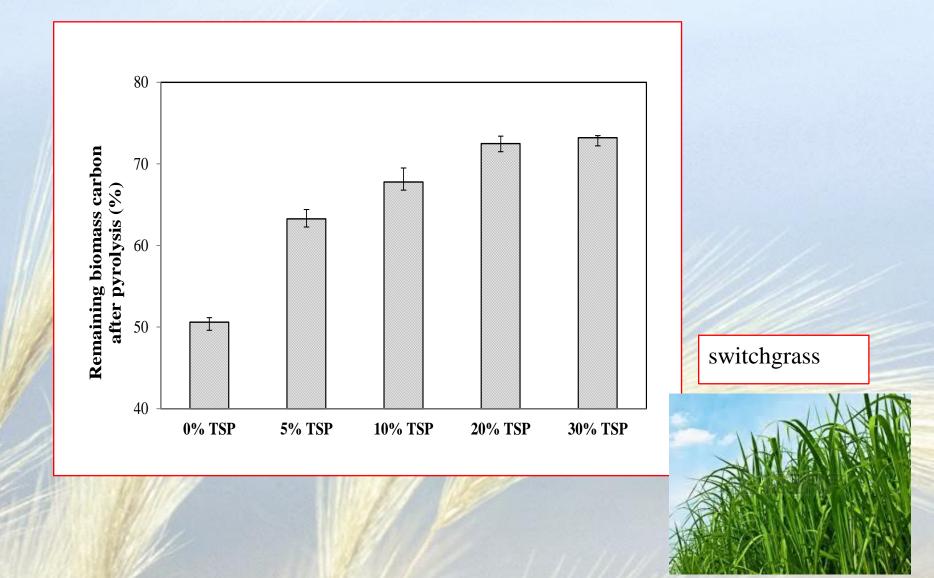
Triple Superphosphate (TSP)

Triple superphosphate (TSP) is P-containing fertilizer. Also, it is an environmentally friendly and low-cost chemical additive. Thus, TSP was chosen as a preferred additive for the following studies.

TSP is produced from "phosphate rock".



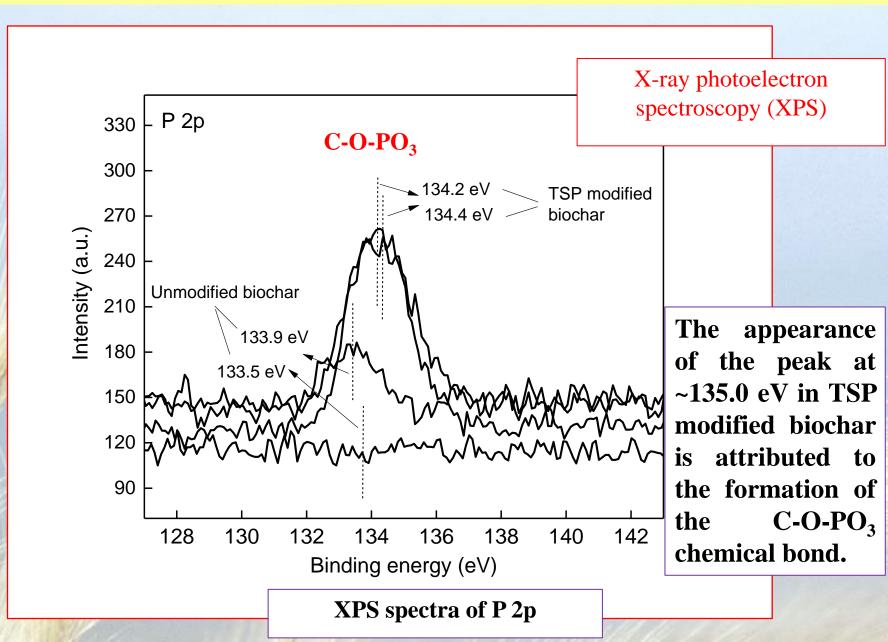
Effect of TSP Addition Amounts on Carbon Retention

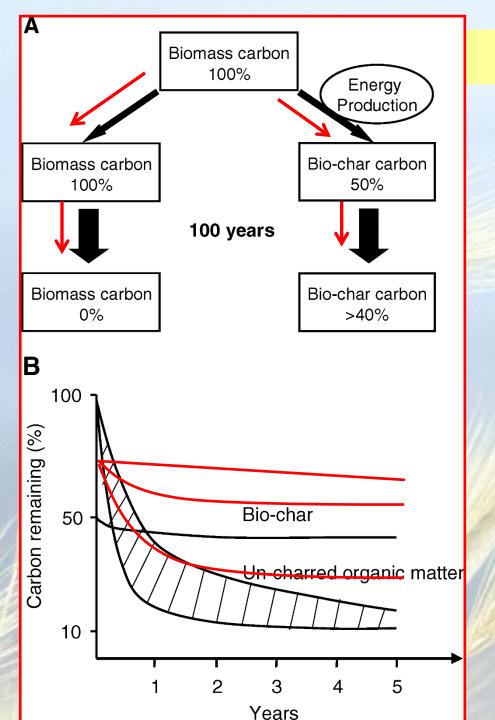


Interaction Mechanism of TSP and Biomass-Carbon During Pyrolysis X-ray diffractometer (XRD) C-P **TSP-BC** PRT-BC H_3BO_4 -BC H₃PO₃-BC BC 15 20 25 30 35 40 45 50 0

A new peak at $2\theta^{\circ}=26.6$ which corresponds to the C-P chemical bond was observed in all P-chemical modified biochars

Interaction Mechanism of TSP and Biomass-Carbon During Pyrolysis



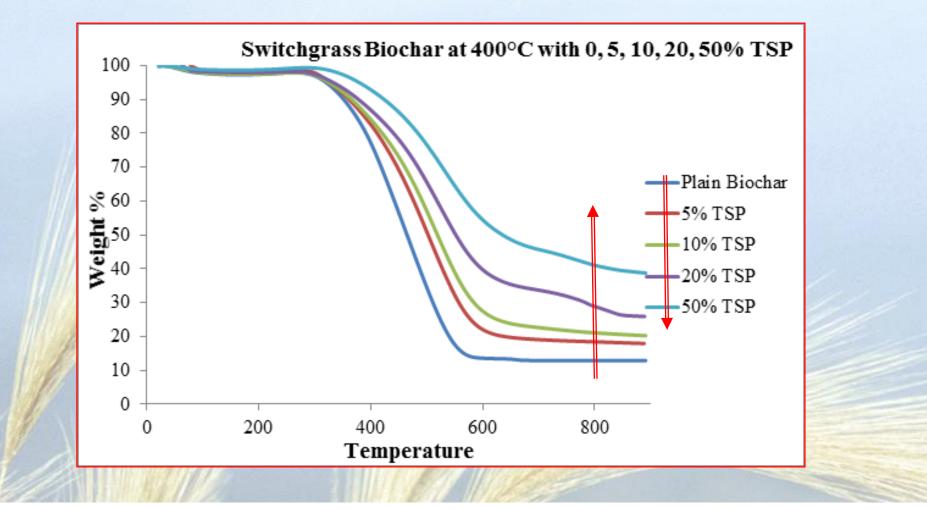


Biochar Stability

Schematics for biomass or biochar remaining after charring and decomposition in soil. (A) C remaining from biomass decomposition after 100 years from IPCC; C remaining after charring or pyrolysis; bio-char C remaining after decomposition. (B) range of biomass C remaining after decomposition of crop residues and estimation of bio-char.

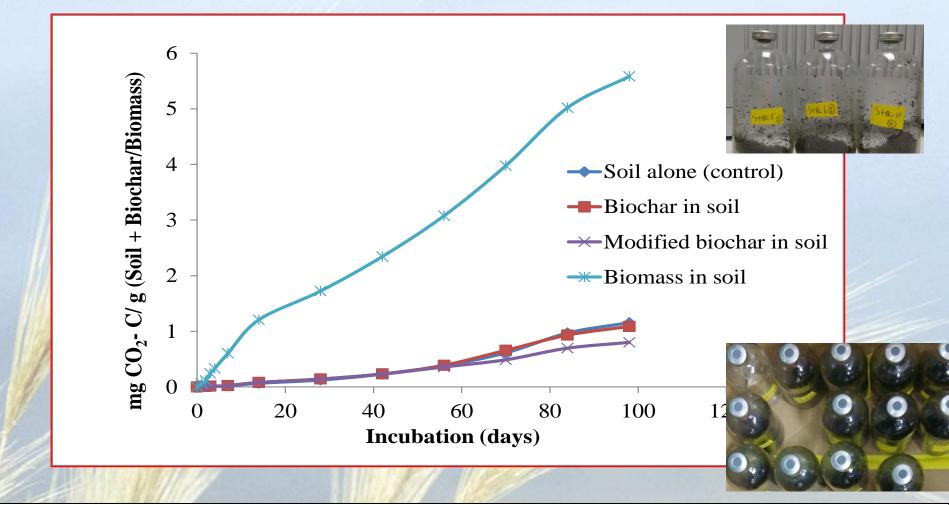
From: Lehmann et al. 2006 in Mitigation and Adaptation Strategies for Global Change

Biochar Thermochemical Stability by TGA



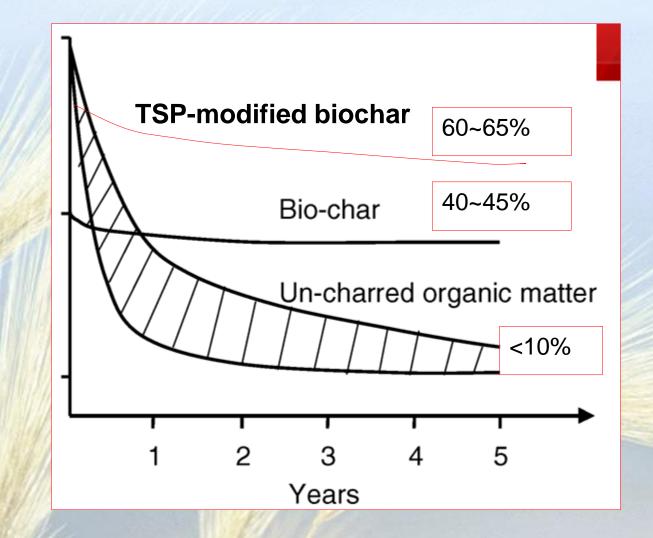
Compared to biochars produced from biomass only, TSP-modified biochars need much higher temperatures for decomposition based on thermogravimetric analysis (TGA), suggesting the TSP- addition could increase biochar thermochemcial stability.

Biological Mineralization of TSP-Modified Biochar in Soil



CO₂-C cumulative emissions from soils amended with biomass, biochar, and TSP-modified biochar produced from switchgrass as well as soil alone (as a control study)

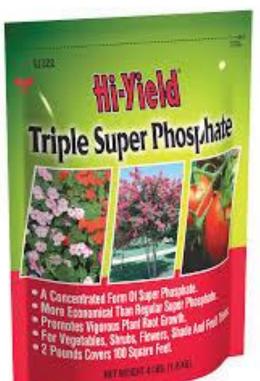
Carbon Footprint Analysis of Biochar



P Leaching from TSP-Modified Biochars

Biomass	Biochar	Leached P (mg) per g solid
Sawdust biochars	BC _{saw}	0.153
	BC _{saw} -TSP	7.07
Switchgrass biochars	BC _{swi}	0.110
	BC _{swi} -TSP	6.18
TSP		101

TSP-Modified Biochar for Slow-Release Fertilizer ??

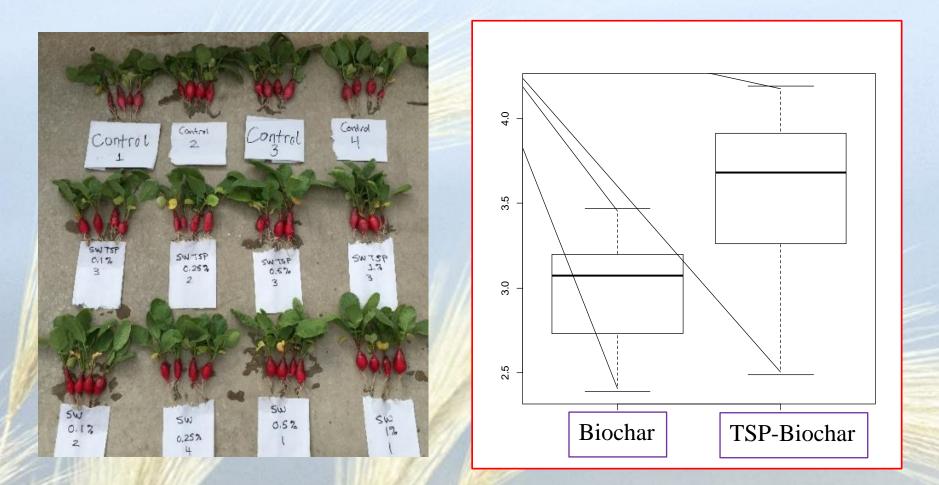




ISTC Slow-Release Fertilizer



TSP-Modified Biochar for Greenhouse Trial



Application rate = 0.25% (significantly different, p=0.01)

Biochar Applications in Soil and Environment

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 - **Carbon sequestration**
 - **Environmental Applications**

Nutrient capture

Emerging contaminant removal



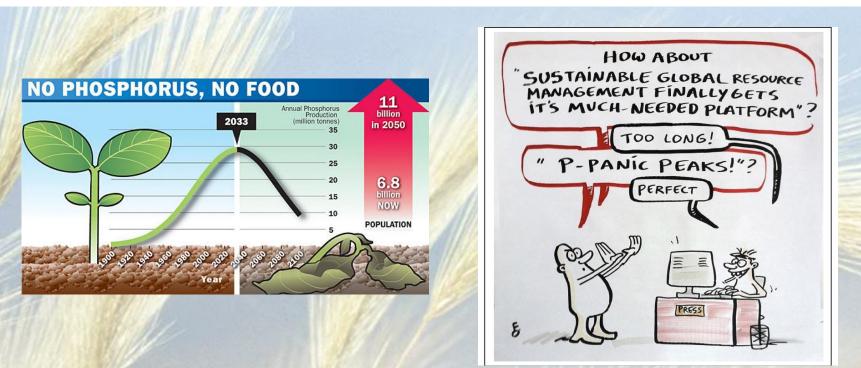
Nutrient Loss from Tile Drainage

- In the Midwestern U.S., subsurface tile drainage systems have been widely used agricultural fields to remove excess water from the soil profile to increase crop production and promote soil conservation.
- → However, tile drainage can deliver large quantities of nutrients, primarily nitrate-nitrogen (NO₃-N) and phosphorus, from agricultural fields into receiving watersheds. It is of particular concern in the Midwest since this nutrient delivery has been identified as a major contributor to the growing hypoxia zone in the Gulf of Mexico. Excess amounts of phosphorus in marine and freshwater systems is often identified as a primary perpetrator for the harmful algal blooms.



Peak Phosphorus

- Recently, phosphorus depletion or "Peak Phosphorus" has been gaining increased public attention since the world is running short of phosphorus ore for chemical fertilizers.
- ➢ It is critical to develop best management practices (BMPs) that can reduce phosphorus losses from fields and recover lost phosphorus for agricultural application.



Research Idea

- > The idea is to produce designer biochars to simultaneously capture ammonium nitrogen (NH_4^+ -N) and phosphate ions from tile drainage water.
- > The nutrient-captured biochars will be used as a slow-release fertilizer to effectively keep nutrients in agricultural loop, minimize their losses, and enhance soil fertility.



Removal Mechanisms of Phosphate & Ammonium by Biochar



Electrostatic adsorption Biochar with negatively charged surface

Analyte Units	Biochar after DI H ₂ O washing	Biochar no washing
	mg/L	mg/L
Sodium*	< 0.6	< 0.6
Potassium*	7.7	15
Calcium*	2.8	3.8
Beryllium	< 0.002	< 0.002
Boron	0.089	0.094
Magnesium	1.5	2.3
Aluminum	0.075	0.084
Silicon	2.0	1.0
Titanium	0.0027	0.0022
Vanadium	< 0.001	< 0.001
Chromium	0.0032	0.0033
Manganese	0.0077	0.0055
Iron*	< 0.1	0.11
<mark>Zeta potential (ζ)</mark>	-21.9±3.8	-22.3±6.9

Designer Biochar Production

- > The surfaces of most biochars are negative charge, so they are generally ineffective to remove phosphorus, especially anionic phosphate ions (PO_4^{3-} , HPO_4^{2-} and $H_2PO_4^{-}$).
- Designer biochars are produced by pyrolysis of biomass pre-treated with calcium-enriched materials lime sludge (main component CaCO₃ with high Mg contents) and gypsum (main component CaSO₄). They are being used as agricultural lime. Lime sludge is a by-product from the softening process in water treatment plants and gypsum is a by-product from power plants.





Projects on Illinois NREC and USEPA

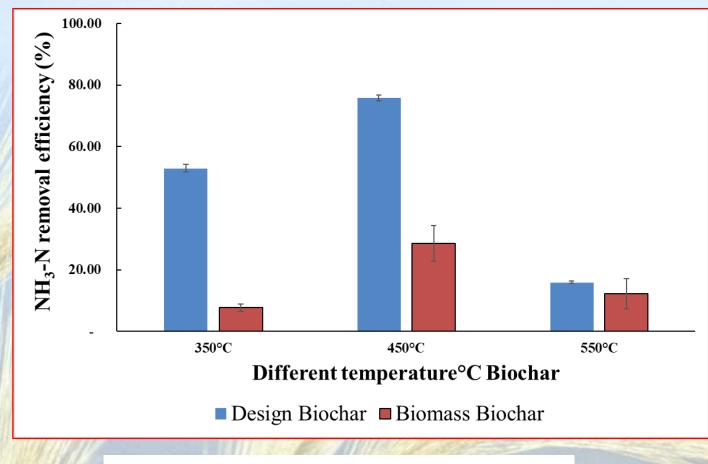


The objectives of these research projects are to generate designer biochars to effectively capture nutrients (especially for dissolved phosphorus) from subsurface tile drainage, recycle nutrient-captured biochars as a slow released fertilizer, and keep phosphorus in the agricultural loop.

Tasks:

- Create designer biochars by pyrolysis of biomass pre-treated with calciumenriched materials (e.g., lime sludge and gypsum)
- Conduct a laboratory experiment to optimize the biochar production conditions by evaluating their sorption capacities for ammonium and phosphate ions.
- Manufacture designer biochars to capture nutrients from subsurface tile drainage by constructing biochar-sorption-channel in fields.
- Recycle nutrient-captured biochars and apply them as a slow-release fertilizer to improve soil quality and crop yields
- Develop and scale-up a

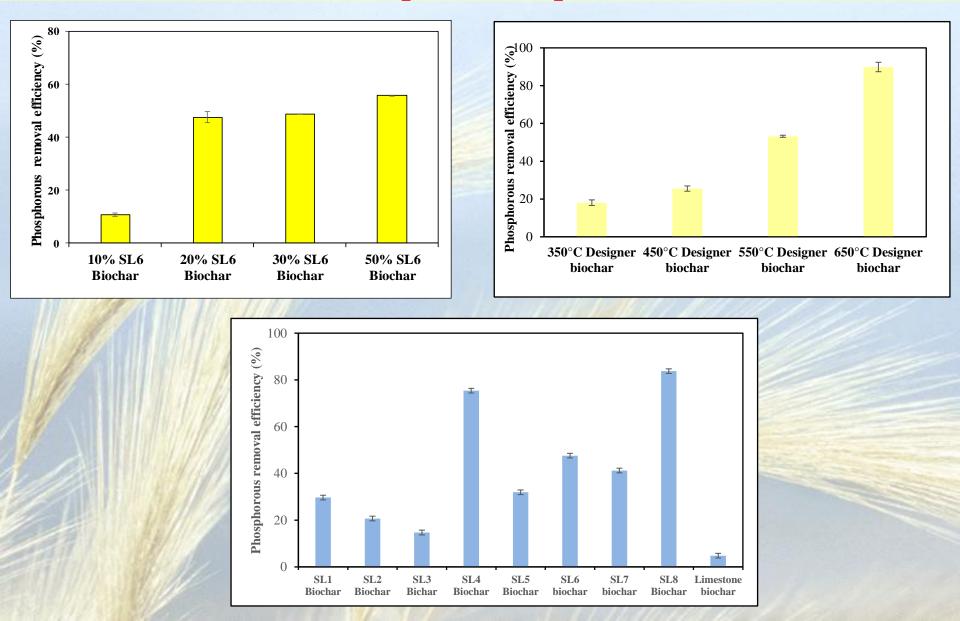
Ammonium Removal by Designer Biochars



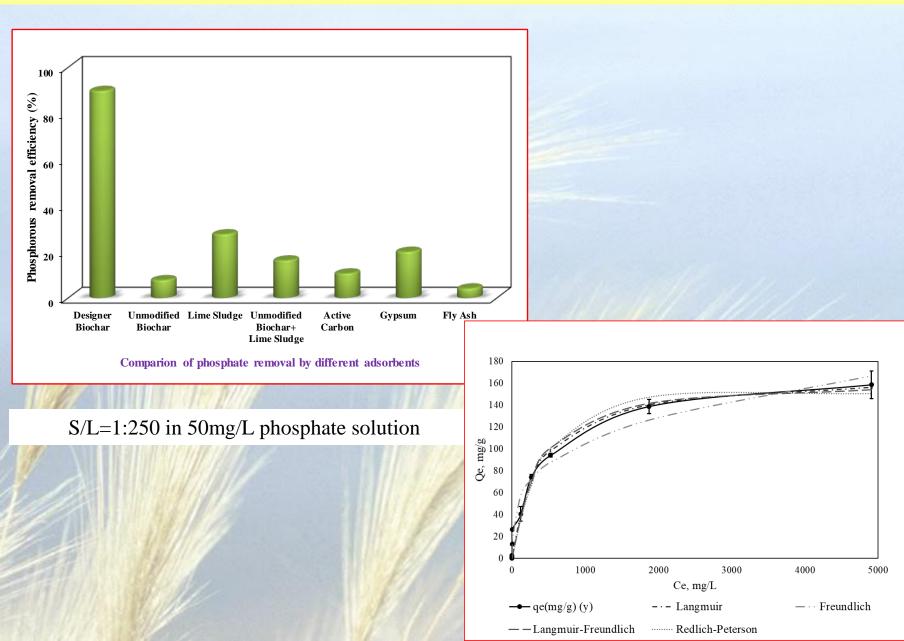
S/L=1:100 in 0.5 mm $NH_4H_2PO_4$ solution

Ammonium sorption capacities of designer biochars produced from different temperatures

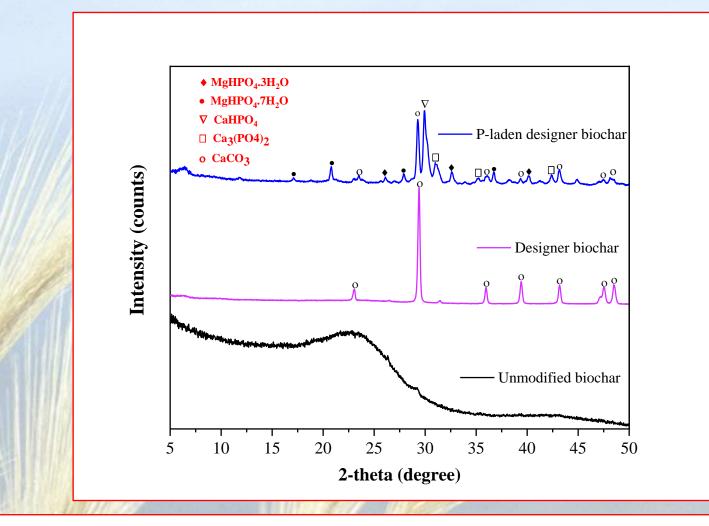
Optimize Designer Biochar Production Conditions to Improve Phosphorus Sorption



Phosphorus Removal by Different Adsorbents



Adsorption Mechanisms — XRD Spectrum



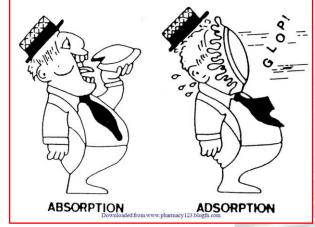
XRD patterns of the unmodified biochar, the designer biochar, and the P-laden designer biochar

Adsorption Mechanisms of Phosphate by Designer Biochar

Adsorption of P could be controlled by multiple mechanisms

- > Intrapartical diffusion on designer biochar (physical adsorption)
- Surface deposition reactions on designer biochar:

$$\begin{split} & Ca^{2+} + PO_4^{3-} + xH_20 \rightarrow Ca_3(PO_4)_2 xH_20 \\ & Mg^{2+} + PO_4^{-3-} + xH_20 \rightarrow Mg_3(PO_4)_2 xH_20 \\ & Ca^{2+} + HPO_4^{-2-} + xH_20 \rightarrow Ca_2HPO_4 xH_20 \\ & Mg^{2+} + HPO_4^{-2-} + xH_20 \rightarrow Mg_2HPO_4 xH_20 \end{split}$$



Activate precipitation of P by designer biochar (i.e., high pH)

Alkalinity is one of the most influential properties for most biochars because their surfaces contain a large amount of alkaline functional groups

 $NH_4^+ + Mg^{2+} + PO_4^{3-} + 6H_2^0 \rightarrow NH_4^- MgPO_4^- 6H_2^0$ (Struvite)

Production of Designer Biochar Pellets





Pyrolysis



Designer Biochar

Bioreactor and P-Sorbing Filter



The field test is being conducted at Fulton County, IL. Currently, three 11.5-acre drainage systems have been installed at the MWRD research site at Fulton County. Each drainage system includes three bioreactor compartments with controlled structure and space to hold P-sorbing filters

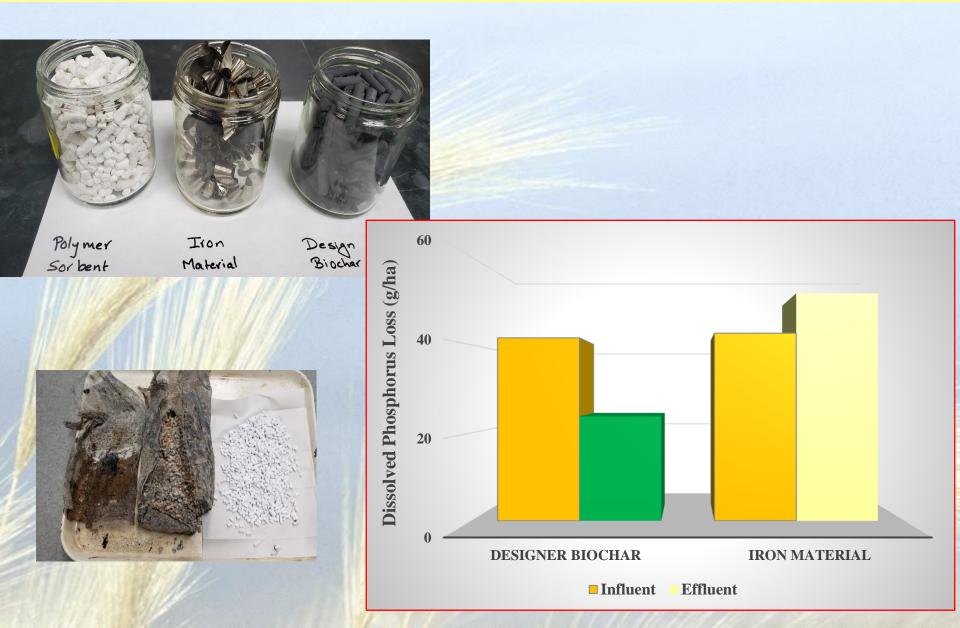
Designer Biochar to Capture Nutrients from Tile Drainage in Fields

Three treatments are being implemented in triplicate in the existing drainage systems:

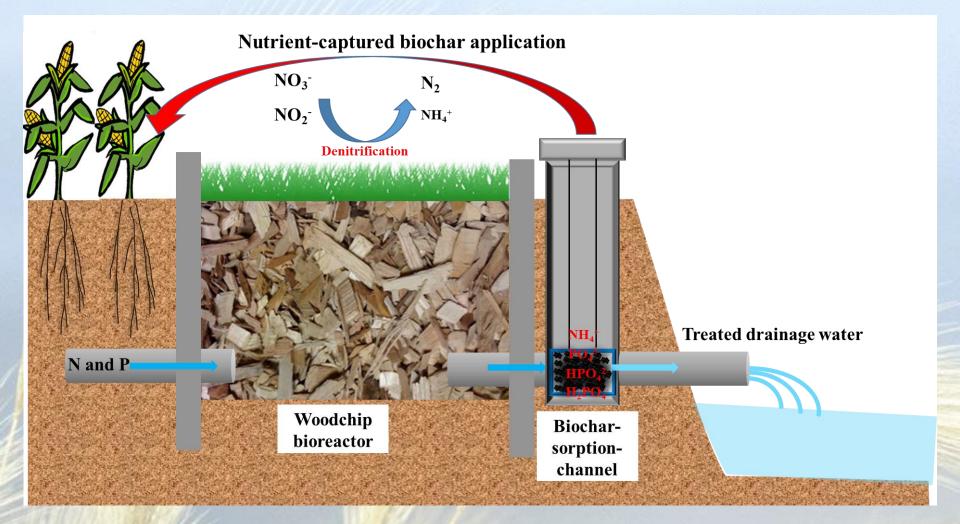
- (1) The designer biochars was packed into the P-sorbing filters
- (2) A commercial polymer-based phosphorus sorbent-RecoNP, which was provided by one of collaborators (Dr. Hundal), was packed into the P-sorbing filters; and
- (3) A slag material was packed into the P-sorbing filters.



Designer Biochar to Capture Nutrients from Tile Drainage in Fields







Biochar-Sorption-Chamber Installation



Nutrient-Laden Biochar for Slow Release Fertilizer





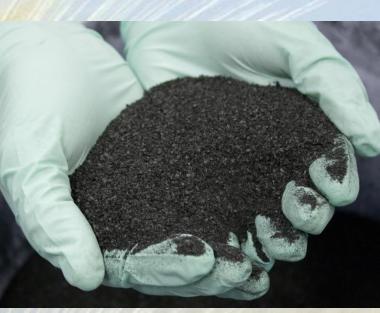
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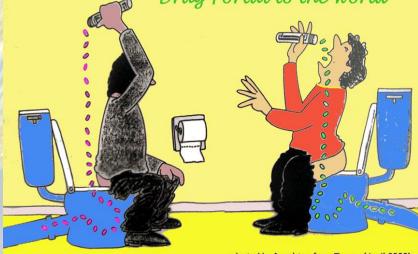
- Soil amendment
 - Carbon sequestration
 - **Environmental Applications**
 - Nutrient capture

* Emerging contaminant removal



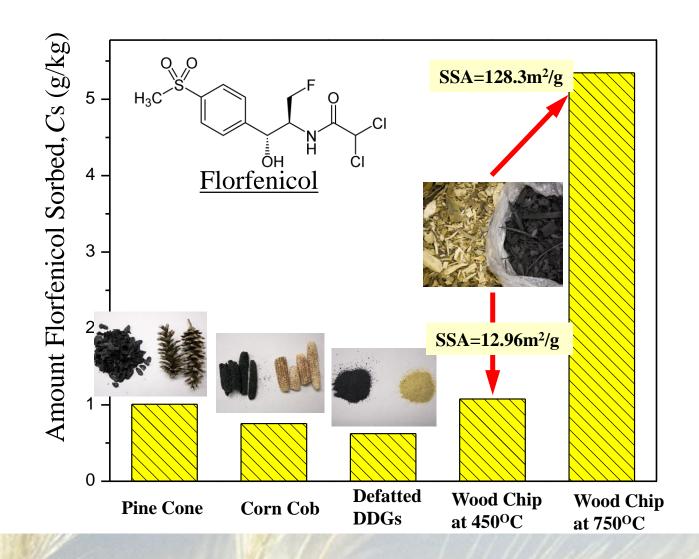
Removal of Pharmaceuticals and Personal Care Products by Biochar

- Currently, pharmaceuticals and personal care products termed PPCPs are receiving great public attentions as emerging contaminants.
- PPCPs have been frequently detected in the lake, river, and stream in the US because they are widely used in human and veterinary clinical practices.
- Because biochar has a high adsorption capacity, it has potential to remove these emerging contaminants
 Drug Portal to the World

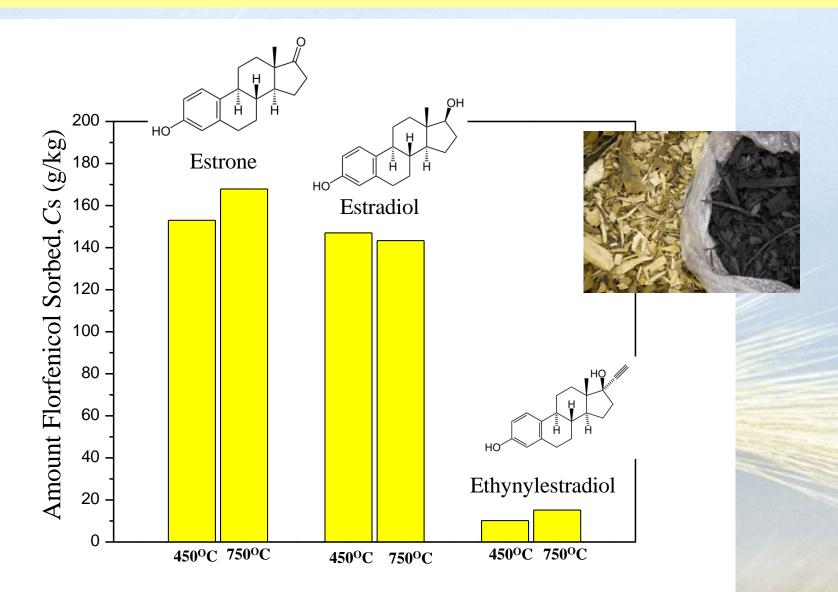


adapted by Daughton from Ternes (April 2000)

Sorption of Florfenicol by Biochars Produced from Different Waste Biomass

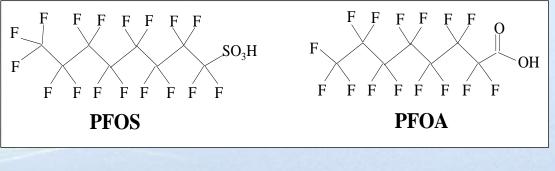


Sorption of Steroid Hormones by Biochars Produced from Wood Waste



Per- and Polyfluoroalkyl Substance (PFAS)

- Aqueous Film Forming Foams
- Stain-Water Resistant Textiles
- Plastics
- Personal Care Products
- Metal Coatings
- Paints
- Cleaning Products
- Oil and Mining Additives
- Food Packaging







PFAS

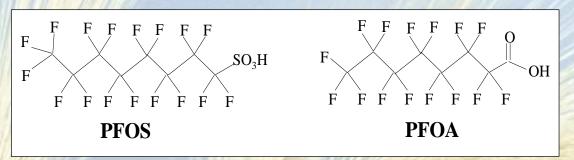
PFAS are "Forever Chemicals". They build up in our bodies and never break down in the environment. Currently, they widely occur in the environment. For example, up to 110 million people may be drinking PFAS-containing water.

PFAS are highly bioaccumulated chemicals. Today nearly all Americans, including newborn babies, have PFAS in their blood. A growing body of science has found that there are potential adverse health impacts associated with PFAS exposure, including liver damage, thyroid disease, decreased fertility, high cholesterol, obesity, hormone suppression and cancer.



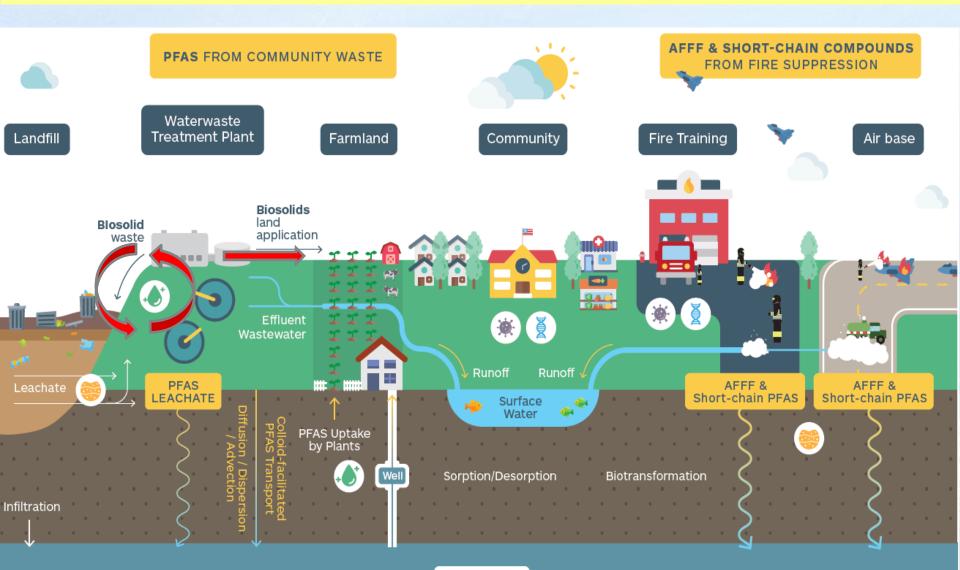
Per- and Polyfluoroalkyl Substance (PFAS)

The occurrence of per- and polyfluoroalkyl substances (PFASs) in the environment, coupled with their known adverse effects on public health, has been recognized as a widespread issue. As a result of legacy use of aqueous film forming foam (AFFF) in firefighting activities, the U.S. Department of Defense (DoD) may have hundreds of sites contaminated with PFASs. It is critical to develop cost-effective and efficient strategies to manage and remediate these PFAS contaminated sites.



In May 2016, the U.S. Environmental Protection Agency (EPA) promulgated drinking water Health Advisory Levels (HALs) for PFOS and PFOA (2, 16). The current HAL for drinking water is 70 ng/L for the sum of PFOS and PFOA, or either compound individually

PFAS Contamination Sources and their Fate/Transport in the Environment



Groundwater

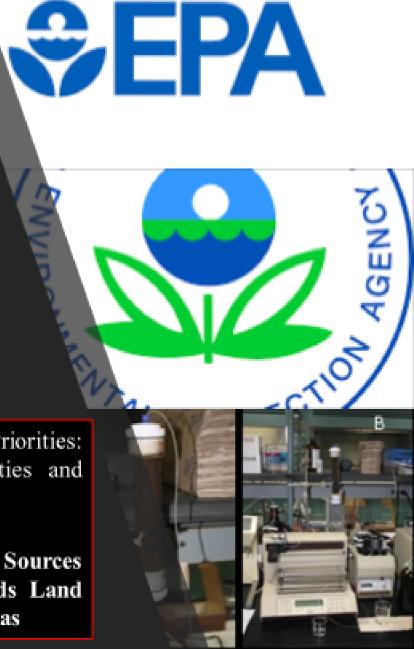
PFAS Fate and Transport Proposals

 Funding Opportunity Title and Number: Practical Methods to Analyze and Treat Emerging Contaminants (PFAS) in Solid Waste, Landfills, soils, and Groundwater to Protect Human Health and protect Human Health and the Environment, EPA-G2018-STAR-B1

 Project Title: Linkage between physiochemical properties of biosolidsassociated PFASs and their behavior in soilplant systems

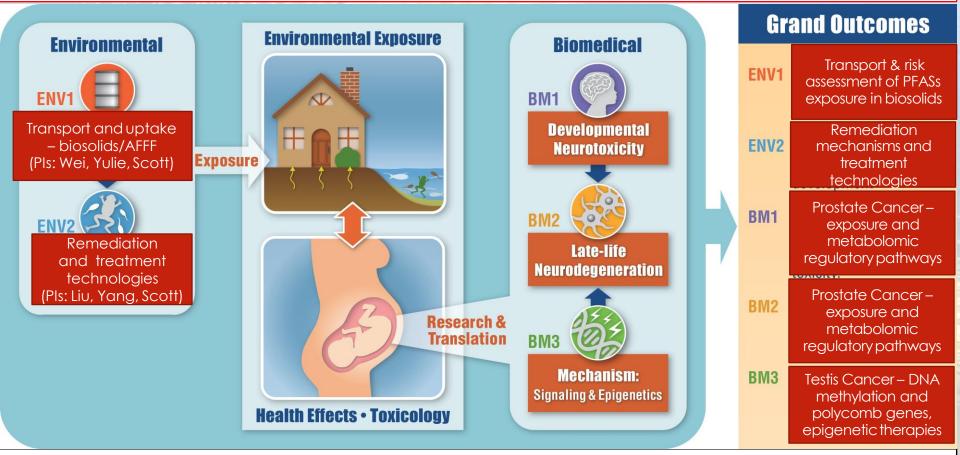
Funding Opportunity Title and Number: National Priorities: Research on PFAS Impacts in Rural Communities and Agricultural Operations, EPA-G2020-ORD-B1

Project Title: Systematic Understanding of PFAS Sources and Mobility to Water Resources from Biosolids Land Application and Water Reuse in the US Rural Areas



NIEHS P42 Superfund Center

The National Institute of Environmental Health Science (NIEHS) proposes the continuation of the Superfund Hazardous Substance Research and Training Program (P42) to address the broad, complex health and environmental issues that arise from hazardous waste sites.



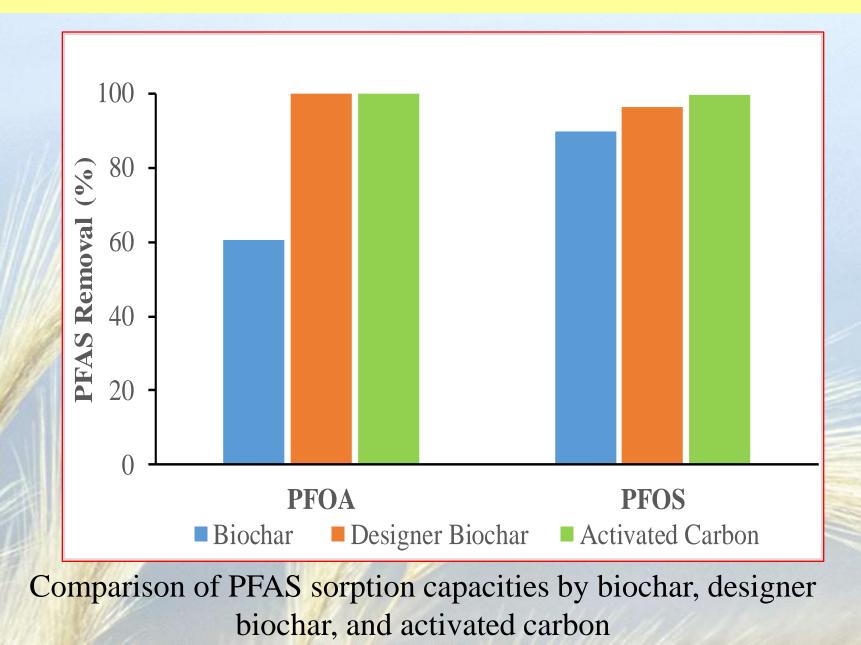
Outline of UIUC's NIEHS Superfund Five Research Cores

Generate a novel biochar to remove PFAS from contaminated water

- Biochar is a carbon-enriched material produced from biomass under a limited supply of oxygen. "Not a high-tech product".
- Biochar is similar in its appearance to charcoal, char, activated carbon, and other black carbon materials.
- The difference of biochar and carbon-rich materials: Biochar is produced with the intent to deliberately apply to soil to:
 - Sequester carbon
 Improve soil quality
 - Improve soil quality

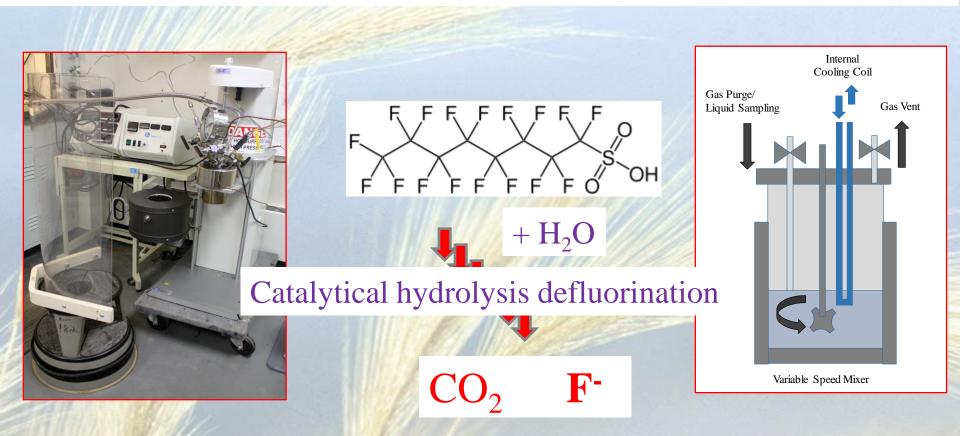






Destruction of PFAS during Designer Biochar Hydrothermal Regeneration

The PFAS-captured biochar will be reactivated using hydrothermal treatment to recover the sorbent under mild regeneration temperatures while at the same time to defluorinate and decompose the PFAS.





Remediation of PFAS Contaminated Biosolids and AFFF-Impacted Soils

Develop innovation mitigation techniques to prevent PFAS leaching from contaminated biosolids and AFFF-impacted soils:

- Biosolid-based biochar: Use of low temperature (<450 °C) pyrolysis to entrap PFAS during biosolid carbonization, stabilize them in biosolid-based biochar, and thereby reduce their availability to leaching and plant uptake.
- Generate an innovative designer biochar and compost it with contaminated biosolids and/or AFFF-impacted soils to constrain the mobility of PFAS and mitigate their leaching

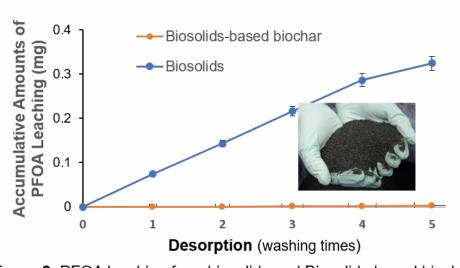
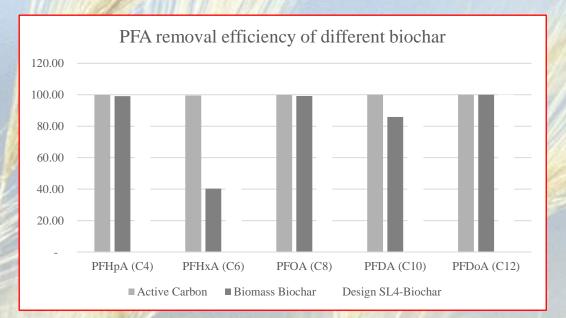


Figure 9. PFOA leaching from biosolids and Biosolids-based biochar



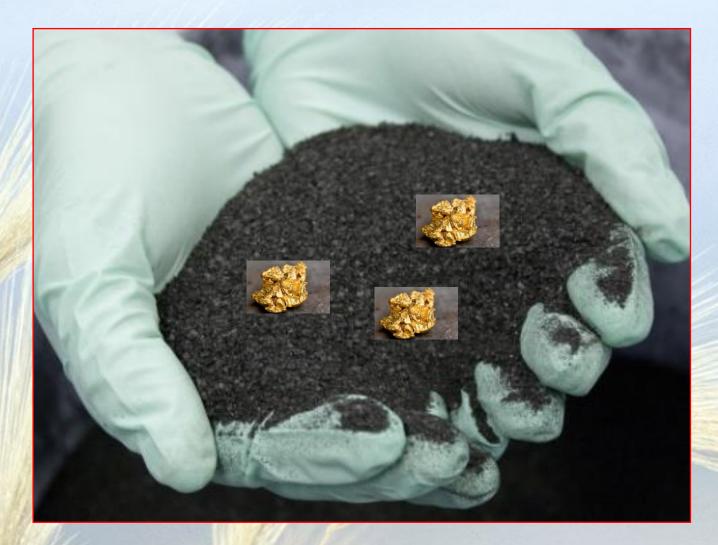
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Summary



What is Biochar?

Biochar is a carbon-enriched material produced from biomass under a limited supply of oxygen. "Not a high-tech product".



Biomass

Pyrolysis

Waste biomass includes:

- Forest and agricultural residues.
- ≻Yard wastes

Bio-oil

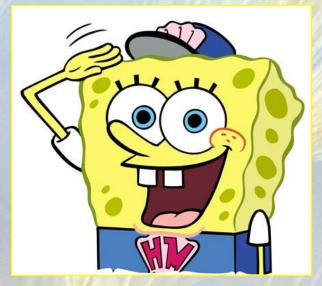
Syngas H₂, CO, CO

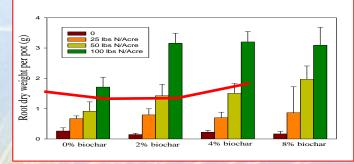
Biochar

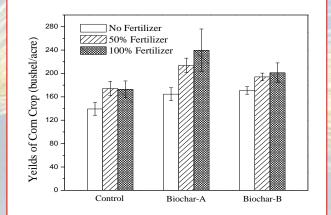
Biochar as a Soil Amendment

Once biochars are added to soil, they can improve soil quality. When used as a soil amendment, biochar can boost soil fertility and improve soil quality by

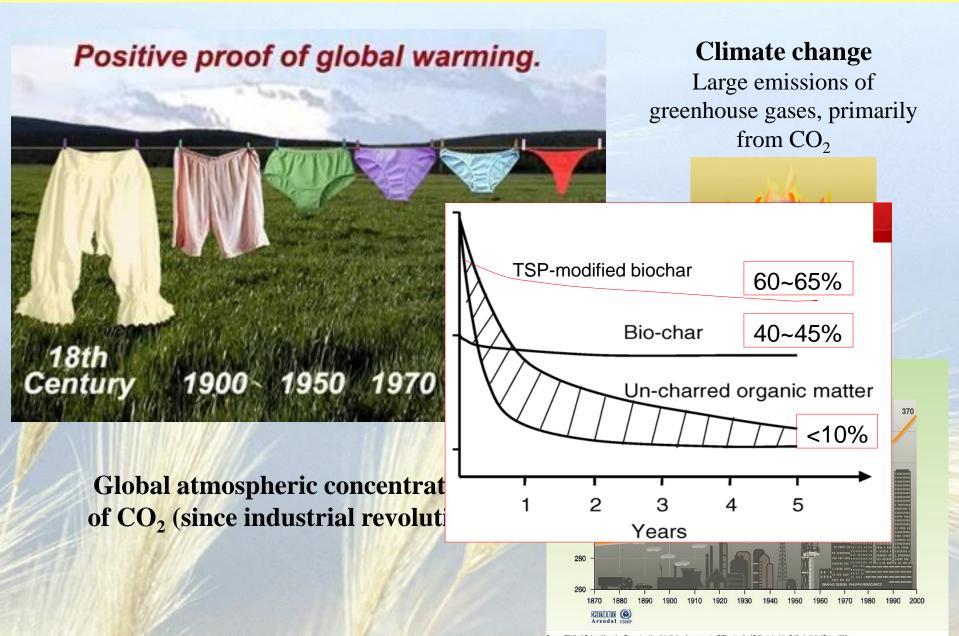
- trapping moisture
- helping the soil hold nutrients
- attracting more beneficial fungi and microbes
- improving cation exchange capacity (CEC)
- raising soil pH
- others....





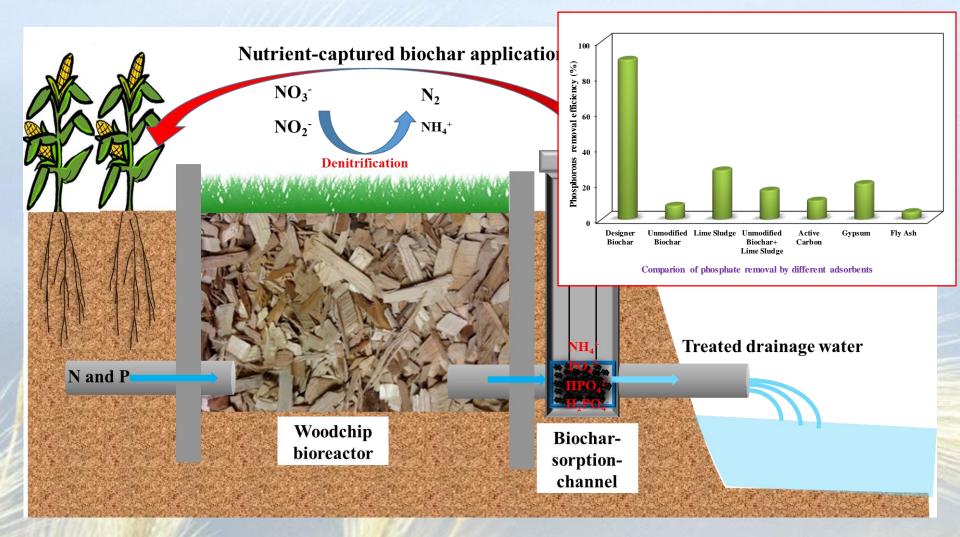


Carbon Sequestration vs Global Warming



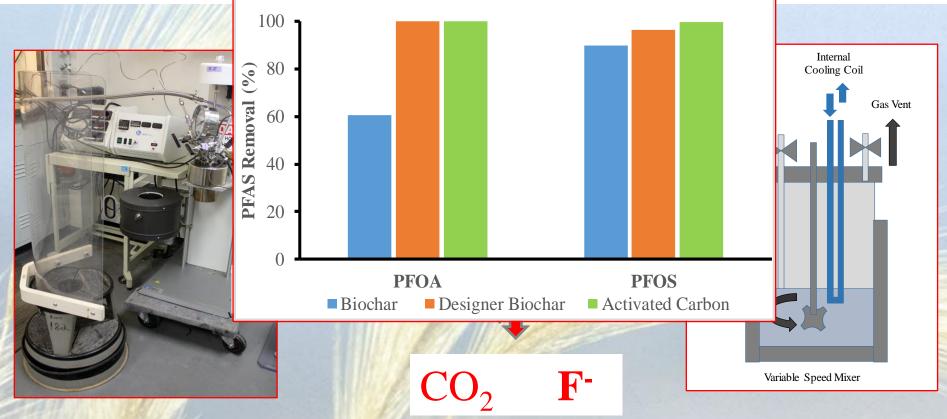
Bioreactor and Biochar-Sorption-Channel





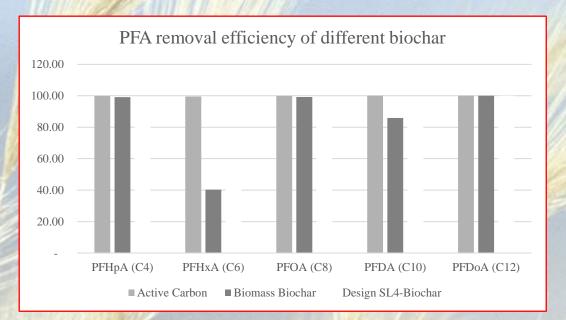
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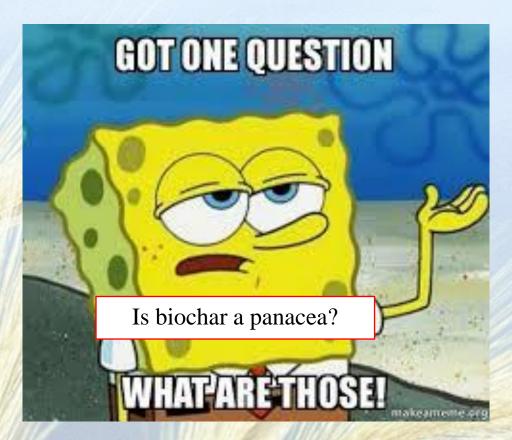
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Questions??



Wei Zheng weizheng@Illinois.edu 217-333-7276