

Quality Assurance Project Plan (Updated in 2022)

Development of a Novel Bioreactor and Biochar-Sorption-Channel (B²) Treatment System to Capture and Recover Nutrients from Tile Drainage

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Grant Number: U.S. Environmental Protection Agency-R840088

A. Project Management

A1. Approvals

Management Approvals:

PI: Wei Zheng Principal Research Scientist	 _____ <i>Signature</i>	11/08/2022 _____ <i>Date</i>
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QA Manager: Lee Green Analytical Chemist	 _____ <i>Signature</i>	11/10/2022 _____ <i>Date</i>
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Quality Assurance:

EPA Project Officer: Sarah Ludwig-Monty	_____ <i>Signature</i>	_____ <i>Date</i>
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EPA Director of Quality Assurance: Michelle Henderson	_____ <i>Signature</i>	_____ <i>Date</i>
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A2. Table of Contents

- A. Project Management..... 1**
 - A1. Approvals..... 1**
 - A2. Table of Contents 2**
 - A3. Distribution List 3**
 - A4. Problem Definition/Background..... 4**
 - A5. Project/Task Description 6**
 - A6. Project/Task Organization 10**
 - A7. Quality Objectives and Criteria for Measurement Data..... 12**
 - A8. Special Training Requirements/Certifications 13**
 - A9. Environmental Concerns and Mitigation 13**
 - A10. Documentation and Records 13**
- B. Measurement / Data Acquisition 15**
 - B1. Sampling Process Design (Experimental Design)..... 15**
 - B2. Sampling Methods Requirements..... 16**
 - B3. Sample Handling and Custody Requirements 17**
 - B4. Analytical Methods 18**
 - B5. Quality Control..... 19**
 - B6. Instrument/Equipment Testing, Inspection, and Maintenance Requirements 20**
 - B7. Instrument Calibration and Frequency 21**
 - B8. Inspection/Acceptance Requirements for Supplies and Consumables..... 21**
 - B9. Data Acquisition Requirements (Non-direct Measurements)..... 22**
 - B10. Data Management 22**
- C. Assessment/Oversight..... 25**
 - C1. Assessments and Response Actions 25**
 - C2. Reports to Management 26**
- D. Data Validation and Usability..... 28**
 - D1. Data Review, Verification, and Validation 28**
 - D2. Verification and Validation Methods..... 28**
 - D3. Reconciliation with User Requirements..... 29**
- E. References 30**

APPENDICES

Appendix A: AMMONIA NITROGEN A023

Appendix B: NITRATE+NITRITE A173

Appendix C: ORTHO-PHOSPHATE A203

A3. Distribution List

The Quality Assurance Project Plan (QAPP) has been submitted to the U.S. Environmental Protection Agency (EPA) project officer. This updated QAPP will be submitted to the USEPA project officer for approval. The original QAPP and this updated revision have also been distributed in electronic format via e-mail to each person signing the approval sheet and to the individuals listed in Section A6 Project/Task Organization, including principal investigator (PI) and co-PIs, quality assurance (QA) manager, laboratory managers, laboratory technicians, and field sampling staff. Individuals such as post-doc researchers and graduate students who participate in this project may request additional copies of the QAPP from personnel listed in Section A6.

An electronic copy of the updated QAPP is posted and publicly available via the website of Illinois Sustainable Technology Center (ISTC) at the University of Illinois at Urbana-Champaign (UIUC): https://www.istc.illinois.edu/research/pollutants/agricultural_chemicals/capturing_recycling_excess_nutrients_from_farmland/

A4. Problem Definition/Background

Problem Statement: Harmful algal blooms (HABs) are blue-green algae that grow out of control and produce toxins, causing catastrophic consequences for ecosystems, human health, and economies [1-5]. Currently, HABs are of growing concern in all 50 states. In the Great Lakes and the Midwestern U.S., HABs typically occur during the warm-weather months of June through October [6-8]. There is an established scientific consensus that excess nutrients in marine and freshwater systems (e.g., the Great Lakes) are primary perpetrators for HABs [6, 7, 9, 10]. This issue is particularly critical in the Midwest because excess nutrients not only jeopardize the local water quality, but also are carried in rivers throughout the states to the Gulf of Mexico and trigger the hypoxic zone [11, 12]. A study conducted in the Mississippi River Basin estimated that agricultural watersheds with a high subsurface drainage density accounted for 70% of the total nutrients delivered to the receiving waters [13]. According to the U.S. Environmental Protection Agency (EPA), for example, four main Corn Belt states (Iowa, Illinois, Nebraska, and Minnesota) contribute about 48% of the nitrogen loads and about 43% of the phosphorus loads that flow into the Gulf of Mexico [14, 15]. Therefore, the EPA's Science Advisory Board set a goal to reduce the exports of excess nutrients to the Mississippi/Atchafalaya River Basin by at least 45% [14].

Bioreactor: To reduce excess nutrient loads into the watersheds, a variety of treatment techniques, conservation strategies, and BMPs have been developed, including constructed wetlands, detention basins, cover crops, riparian buffers, and denitrifying bioreactors [16-22]. Denitrifying bioreactors have been proven to be a cost-effective, practical, and sustainable solution to reduce nitrates from tile-drained agricultural fields in the Midwest [23, 24]. In general, a subsurface bioreactor is a buried trench with woodchips, or some other carbon source, through which the tile water flows before entering a surface water body [25, 26]. Naturally occurring soil microorganisms colonizing the woodchips would convert nitrate-nitrogen ($\text{NO}_3\text{-N}$) into inert dinitrogen gas (N_2) under anaerobic conditions. Denitrifying bioreactors as an edge-of-field practice can not only remove $\text{NO}_3\text{-N}$ from agricultural drainage water, but also treat mine drainage and landscape drainage waters (e.g., golf courses and lawns) [27, 28].

In the bioreactor system, four processes are responsible for the removal of $\text{NO}_3\text{-N}$: (1) denitrification; (2) dissimilatory nitrate reduction to ammonium/ammonia (DNRA); (3) ammonium oxidation; and (4) biomass assimilation [27]. Previous studies have clearly shown that denitrification is the most significant process in bioreactor systems. Most of the $\text{NO}_3\text{-N}$ converts to N_2 with a relatively low production of ammonium-nitrogen ($\text{NH}_4\text{-N}$) and nitrous oxide (N_2O) [16, 27, 29, 30]. The production of $\text{NH}_4\text{-N}$ in the bioreactor system is an undesirable pathway for $\text{NO}_3\text{-N}$ denitrification, where nitrate (NO_3^-) is sequentially reduced to nitrite (NO_2^-) and in turn to ammonium/ammonia ($\text{NH}_4^+/\text{NH}_3$). In addition to DNRA, $\text{NH}_4\text{-N}$ may be produced by mineralizing organic matter in the bioreactors [27, 29]. Thus, the concentrations of $\text{NH}_4\text{-N}$ are often elevated in the drainage water following bioreactor treatments [22, 27, 29, 31], leading to a potential risk of eutrophication since $\text{NH}_4\text{-N}$ is more easily incorporated into algal biomass than $\text{NO}_3\text{-N}$. Besides, woodchip bioreactors usually do not significantly affect phosphorus removal [16, 32]. At worst, our previous study disclosed that the concentrations of phosphorus could be increased after biomass bioreactors, suggesting that some organic phosphorus could be decomposed in bioreactors.

Phosphorus losses through subsurface tile drainage were once thought to be insignificant compared to its surface runoff [33, 34]. But since the mid-1990s, tile drainage has been recognized as a significant pathway for phosphorus transport because of the broad application of subsurface drainage systems and extensive adoption of no-till farming [33, 35]. From the perspective of plant growth and maturity, however, phosphorus is an essential and vital component. Recently, phosphorus depletion or "peak phosphorus" has gained increased public attention since the world is running short of phosphorus ore for chemical fertilizers [36-38]. Therefore, it is critical to develop best management practices (BMPs) that can reduce phosphorus losses to mitigate contamination, and simultaneously recover phosphorus for its agricultural application.

Biochar: Biochar is a carbon-rich material that may persist in soils for millennia because it is highly resistant to microbial decomposition. Recently, the application of biochar into soils has gained recognition as a viable solution to reduce the growing levels of CO₂ in the atmosphere [39, 40]. In addition to carbon sequestration, other benefits of applying biochar to field soils include acting as: (i) an adsorbent to increase the soil's sorption capacity for plant nutrients and agricultural chemicals; (ii) a carrier to release nutrients slowly; (iii) a relatively low-density material to lower the bulk density of high-clay soil; and (iv) a liming agent to offset the acidification of soils [40-42]. Our previous studies suggested that biochar can not only strongly adsorb cationic nutrients such as NH₄⁺ through an electrostatic adsorption mechanism [43], but it also has a high sorption capacity for other chemical contaminants, such as pesticides and antibiotics [40, 44]. Compared to soil organic matter, biochars have a greater affinity for organic compounds due to their highly carbonaceous and aromatic nature and relatively high surface area. It has been reported that biochar could be >2,000 times more effective than soils in sorbing pesticides [45, 46]. Thus, biochar soil amendments are likely to reduce the bioavailability of chemical contaminants, thereby impeding them from leaching into groundwater and decreasing the potential for plant uptake [46, 47].

The surfaces of most biochars are negatively charged, so they are generally ineffective in removing anions such as NO₃⁻, NO₂⁻, and dissolved phosphorus (e.g., PO₄³⁻, HPO₄²⁻, and H₂PO₄⁻) [32, 43]. However, some biochars produced from special biomass containing high calcium and magnesium components showed a high phosphorus-sorption capacity [43, 48, 49]. Recently, researchers attempted to enhance nutrient removal rates by directly adding biochars into the woodchip bioreactors, but the results are mixed and inconsistent [16, 26, 50, 51]. Some studies showed that the additions of biochar to woodchip bioreactors resulted in a statistically significant increase in NO₃-N removal [52, 53], suggesting biochars can supplement some carbon matters to help denitrification in the bioreactors. By contrast, some studies indicated that biochar added to the bioreactors had limited effects [26] or even failed [50] to enhance nutrient removal since woodchip bioreactors have had sufficient carbon sources to support microorganisms for denitrification. In addition, the life cycles of the woodchips and biochars are different, so it is impossible to take them out of the bioreactors to recover the adsorbed nutrients (especially for dissolved phosphorus).

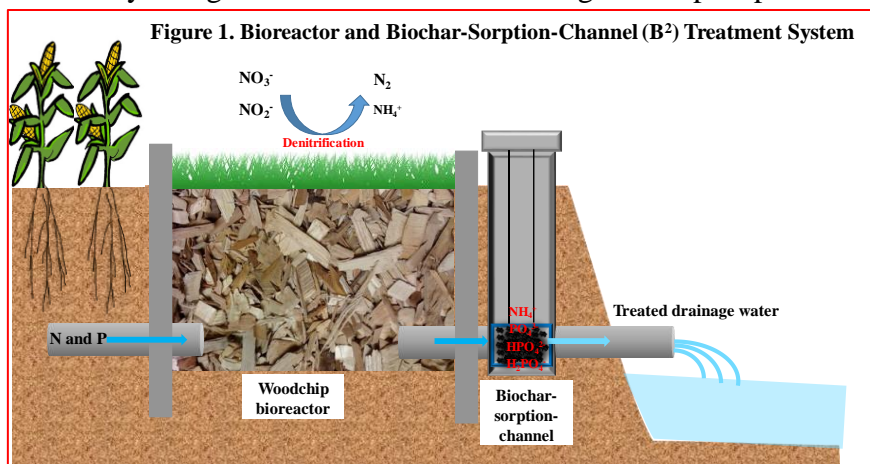
Perspective: We have completed several projects related to biochar application in the environment and agriculture, including carbon sequestration and soil amendment. We are currently conducting a project funded by the Illinois Nutrient Research and Education Council (NREC) to design special biochars to capture nutrient losses from tile drainage [43, 54]. The project aims to generate designer biochars to effectively capture phosphorus (dissolved phosphorus and total phosphorus) from subsurface tile drainage. In the NREC project, we have generated some designer biochars

with high capacities for holding anions such as dissolved phosphorus. These designer biochars are produced from wood biomass treated with a lime sludge before pyrolysis. Lime sludge is a by-product of drinking water treatment and can be used as agricultural lime to neutralize soil acidity. The preliminary study suggests that the pretreatment of biomass with lime sludge for biochar production has a significant synergistic effect on phosphate sorption. In addition, a preliminary study also showed that the designer biochars have a higher sorption capacity on $\text{NH}_4\text{-N}$ compared to the unmodified biochar, suggesting the pretreatment of lime sludge may increase the cation exchange capacity of the designer biochar.

This project will optimize the production conditions to generate the most cost-effective and efficient designer biochars to capture phosphorus and $\text{NH}_4\text{-N}$ from drainage water simultaneously. The nutrient-captured biochars will be applied in the fields to recover the nutrients and thus keep them in a closed agricultural loop. More significantly, we will integrate designer biochar and woodchip bioreactor treatment techniques to comprehensively reduce the losses of both nitrogen and phosphorus nutrients from tile drainage systems.

A5. Project/Task Description

This project is to develop and scale up an innovative bioreactor and biochar-sorption-channel (B^2) treatment system (Figure 1) to effectively mitigate the losses of both nitrogen and phosphorus nutrients from subsurface drainage water, recycle nutrient-captured biochars as a slow-release fertilizer, and keep nutrients in a closed agricultural loop. The project encompasses a series of laboratory and field studies to resolve the nutrient pollution, and thereby diminish the occurrence of HABs. **Seven tasks** will be implemented in this project.



Task 1. Optimization of Designer Biochar Production

In this project, we will pretreat two common types of biomass using lime sludge collected from drinking water plants. We will use a slow pyrolysis plant developed in our laboratory to generate a series of designer biochars under different production conditions. A batch experiment will be conducted to evaluate the adsorption capacities of all produced biochars to $\text{NH}_4\text{-N}$ and dissolved phosphorus. According to the laboratory results, we will select the most optimal production conditions to manufacture the most cost-effective and efficient designer biochars for the following field demonstration study. In brief, the selected biomass will be mixed with the selected lime sludge based on the optimal ratios. Then, the pretreated biomass will be pelleted using a commercial biomass pelletizer. Finally, the pellets will be pyrolyzed to manufacture the most

efficient and cost-effective designer biochar under the optimal production conditions. To manufacture designer biochar pellets, we will need to rent a commercial pelletizer and a rotary kiln.

Task 2. Develop and Demonstrate B² Treatment System in a Field Trial

A B² treatment system (Figure 1) will be set up at the University of Illinois Dairy Farm (1-acre field) in Urbana, Illinois. This task will use the existing tile drainage system to develop a B² nutrient treatment system and confirm the proposed technology on nutrient removal in a field trial. Co-PI Cooke will work with some drainage companies to design and build a woodchip bioreactor, removable biochar filters, and a biochar-sorption-channel. The woodchip bioreactor will be designed as a subsurface system with ~1.5 m deep trench. A two-stage biochar-sorption-channel system that includes two successive tubes (1.2m x 0.15m for each) (Figure 2) will be constructed and installed behind a woodchip bioreactor. The designer biochar pellets will be packed into two sorption tubes and put into the biochar-sorption-channel (Figure 2).

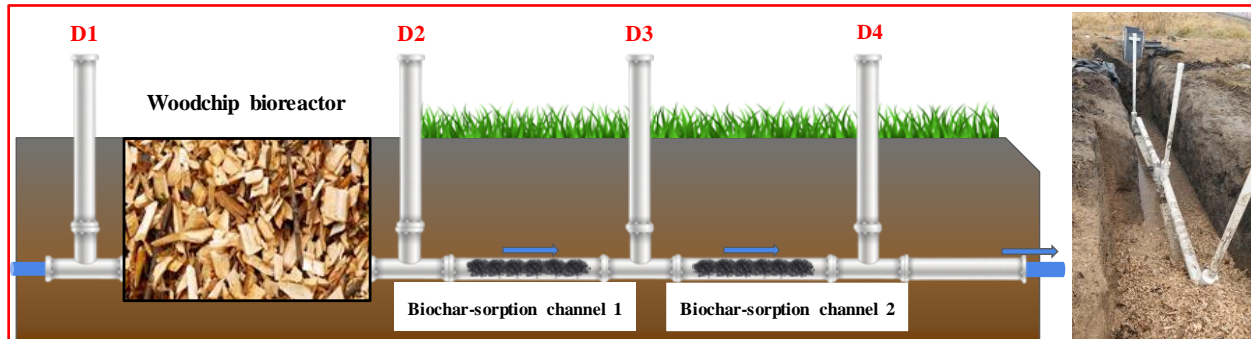


Figure 2. Biochar-sorption-channel with refillable biochar sorption filters

This field study will be carried out for six consecutive months. Water samples will be collected from influent (before the woodchip bioreactor), intermediate solution (after the woodchip bioreactor), and effluents (after biochar-sorption-channel) to determine the effectiveness of the bioreactor and designer biochars on the removal of NO₃-N, NH₄-N, dissolved phosphorus, and total phosphorus. Drainage water samples will be collected two times per week and within 24 hours of a rain event equaling or exceeding 0.5 inches. All collected water will be immediately shipped to the Water Quality Laboratory (WQL) in the Agricultural Engineering Department (ABE) at UIUC for analysis. In addition, the designer biochars will be replaced once they reach the sorption capacities based on the monitoring results.

Task 3. Develop and Demonstrate a Scale-up B² Nutrient Treatment System

To cover a larger field drainage system and obtain sufficient nutrient-captured biochar for fertilizer testing, the B² nutrient treatment system will be scaled up, allowing it to treat more drainage water receiving from a larger agricultural field. Currently, we are conducting a project funded by the IL NREC to use designer biochar to capture dissolved phosphorus from tile drainage water in an agricultural field located on the Metropolitan Water Reclamation District of Greater Chicago (MWRD) Nutrient Loss Reduction Research Site in Fulton County, Illinois [54]. In this project, we will use the well-developed tile drainage systems at the MWRD's research site to scale-up the

B² nutrient treatment technology. The scale-up B² system will be able to treat drainage water from fields that are up to 20 acres. According to the previous hydrology data, the woodchip bioreactor (25.0 m long, 5.0 m wide, and 1.5 deep) will be installed at the edge of tile-drained fields. A biochar-sorption-channel system (Figure 3), including a refillable biochar sorption chamber, will be built and attached to the woodchip bioreactor. The biochar sorption chamber will be filled with designer biochar pellets and installed into the biochar-sorption-channel. The designer biochars will be replaced using a portable winch (Figure 3) once their sorption capacities are saturated.

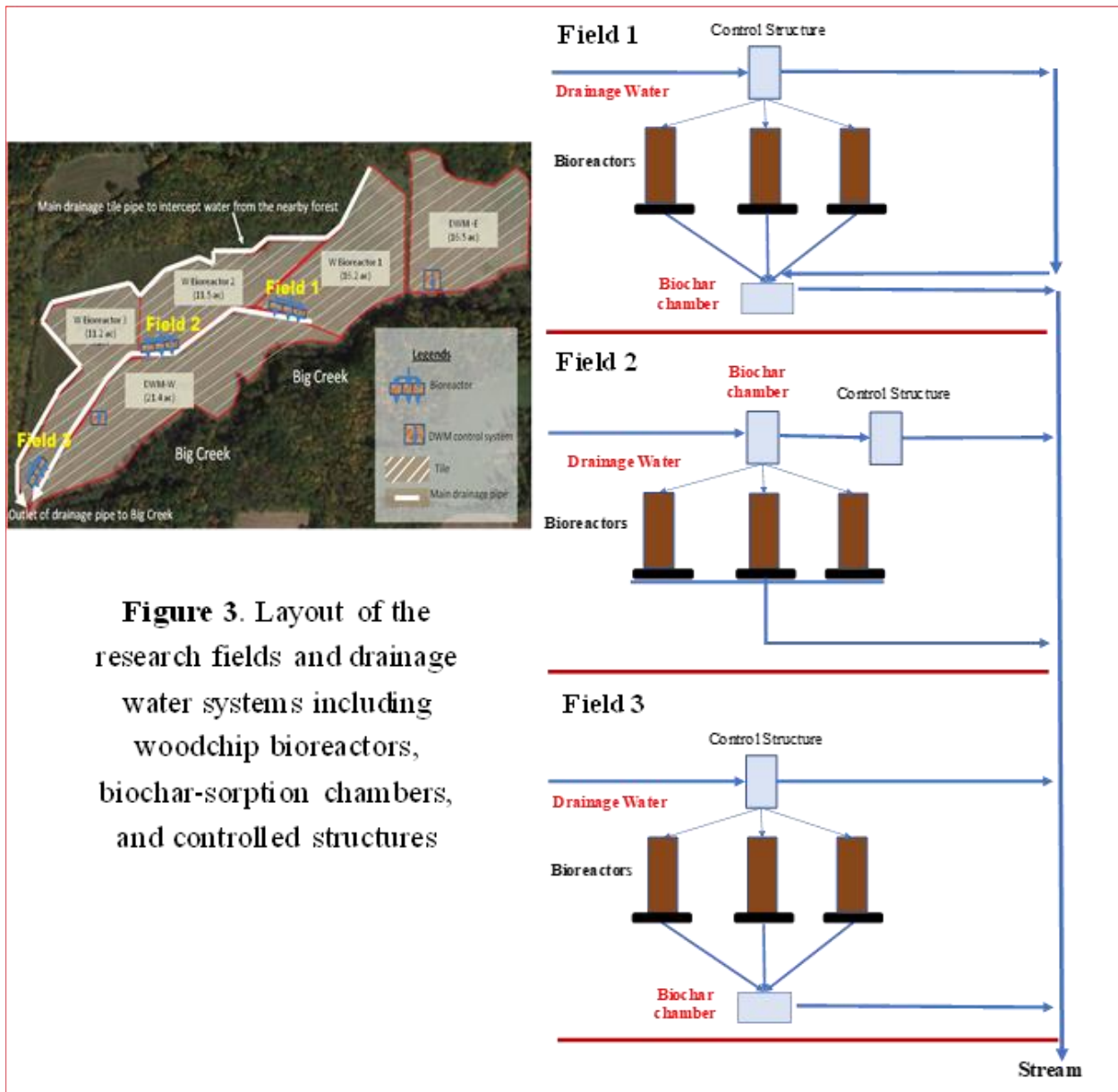


Figure 3. Layout of the research fields and drainage water systems including woodchip bioreactors, biochar-sorption chambers, and controlled structures

Figure 3. A scale-up biochar-sorption-channel with refillable biochar sorption chamber

Similar to the field trial (*Task 2*), water samples will be collected from influent (before the woodchip bioreactor), intermediate solution (after the woodchip bioreactor), and effluent (after the biochar-sorption-channel) to determine the effectiveness of the bioreactor and designer biochars

on the removal of NO₃-N, NH₄-N, dissolved phosphorus, and total phosphorus. According to previous hydrology data, this field study will be carried out for nine consecutive months since no drainage water flows from July to September at the selected field site. Drainage water samples will be collected weekly and within 24 hours of a rain event equaling or exceeding 0.5 inches. All collected water samples will be immediately shipped to WQL in ABE for analysis. In addition, a weather station with a satellite-controlled system, accessed via a computer or handheld device with internet connectivity, has been installed to collect meteorological information. It has the capability to monitor flow, water table level, and rainfall.

Task 4. Evaluate the B² Nutrient Treatment System by Demonstrating a Scale-up Field Study

The scale-up field study will be conducted in a commercial corn production farm in Champaign or Fulton County, Illinois, in collaboration with a local farmer. The purpose of this task is to determine treatment efficiency using multiple B² nutrient treatment systems at a large field scale, explore its application feasibility in commercial agricultural farms, and thereby evaluate the possibility to scale up this new technology on nutrient control at a watershed level. Multiple (up to 5) B² nutrient treatment systems developed in *Task 3* will be installed along the edges of 100-acre tile-drained fields. Similarly, water samples will be collected from each B² system, including influent, intermediate solution, and effluent samples. All water samples will be collected weekly or bi-weekly and within 24 hours of a rain event equaling or exceeding 0.5 inches. This field study will be carried out for nine consecutive months since there is usually no drainage water during summertime (July to September). All collected samples will be immediately shipped to the WQL at UIUC/ABE to analyze NO₃-N, NH₄-N, dissolved phosphorus, and total phosphorus. Similarly, the designer biochars will be replaced using a portable winch (Figure 3) once they reach the sorption capacities.

Task 5. Recycle Nutrient-Captured Biochar as a Slow-Released Fertilizer

A field study will be carried out to demonstrate to researchers, farmers, regulators, the agriculture community, and other potentially interested parties the feasibility and efficiency of the nutrient-captured biochars as a slow-released fertilizer. The demonstration experiment will be conducted in the same commercial corn production fields in Champaign County, Illinois. The nutrient-captured biochars will be withdrawn from the biochar-sorption-channels after they reach their sorption capacities. They will be mixed with the topsoil (0~10 cm) at an application rate of 10 t/ha. Three treatments related to chemical fertilizer application rates (0, 50%, and 100% of normal fertilizer application rate) will be performed in the field soils with and without a biochar amendment. The detailed experimental procedure will follow our previous field studies [43, 56, 57].

Task 6. Cost-Benefit Analysis of B² Nutrient Treatment System

The cost-benefit analysis concerning the B² nutrient treatment system for nutrient capture will be evaluated compared to various existing treatment technologies. Currently, several agricultural conservation practices and BMPs are being conducted at the MWRD's research site, which provides excellent opportunities to accurately and effectively assess the B² nutrient treatment system compared to these existing management practices. The cost-benefit analysis concerning designer biochars for nutrient capture and recycling will be evaluated compared to various nutrient

recovery techniques. The evaluation includes two categories. One is the application feasibility and treatment efficiency of the B² system on the control of nutrient losses in subsurface tile drainage systems. The other category is cost. Ecosystem Exchange Services will provide cost-benefit analyses for innovative technology as a third party.

Task 7. Extension/Outreach Activities

Knowledge gained from this study will be incorporated into the Online Drainage Guide developed and maintained by co-PI Cooke, who has worked with the Natural Resource Conservation Service (NRCS) to develop design standards for other practices, such as drainage water management and bioreactors. Results from this study will also be communicated to farmers and the public through collaboration with the Illinois Farm Bureau and with the assistance of the University of Illinois Extension, Soil and Water Conservation Districts, and the NRCS. Outreach activities to disseminate our findings will include press releases for the popular media, presentations at scientific meetings, reports, and published articles in scholarly journals. Co-PIs Cooke and Guzman conduct annual drainage workshops for contractors and will incorporate information from this project into that course material and their UIUC course content. Co-PI Oladeji and his research group will conduct tours of the MWRD research facility. Field studies in this project will be conducted at the University research farm, the MWRD research site, and the commercial corn production farm. All of them are accessible to local and regional agricultural communities and other key citizen groups influencing land management. We will arrange field days at the facility to demonstrate the innovative B² nutrient treatment system to farmers, the agricultural community, and the public.

Schedule: This is a three-year project. Table 1 summarizes the project tasks and their timeline.

Table 1: Project Milestones and Anticipated Completion Dates

Activity	Year 1			Year 2			Year 3		
Task 1. Designer Biochar Optimization and Production	■	■	■	■	■	■			
Task 2. Develop B ² Treatment System in a Trial Field		■	■	■					
Task 3. Demonstrate a Scale-up B ² Treatment System				■	■	■			
Task 4. Evaluate the B ² System using a Scale-up Field Study					■	■	■	■	■
Task 5. Recycle Nutrient-Captured Biochar as a Fertilizer							■	■	■
Task 6. Cost-Benefit Analysis of B ² System								■	■
Task 7. Extension/Outreach Activities		■	■	■	■	■	■	■	■
QAPP and Annual Progress Reports	■		■			■			
Final Report Submission									■

A6. Project/Task Organization

The PI, Dr. Wei Zheng, is a principal research scientist at ISTC at UIUC. He is responsible for administering the overall project, coordinating and executing the project tasks (Tasks 1-7), and overseeing the preparation of annual and final reports. Dr. Richard Cooke is a professor in ABE at UIUC. As a co-PI, he is responsible for establishing B² systems and leading field work (Tasks 2,

3, 4) as well as extension/outreach activities (Task 7). Dr. Jorge Guzman is an assistant research professor in ABE at UIUC. As co-PI, he will assist Dr. Cooke to manage all field studies and extension activities (Tasks 2, 3, 4 and 7). In addition, he is responsible for the application of nutrient-captured biochar as a slow-release fertilizer (Task 6). Dr. Nandakshihore Rajagopalan is a Illinois State Scientist (research engineer) at ISTC at UIUC. As co-PI, he is responsible for biomass pelletizing and biochar production (Task 1). Dr. Olawale Oladeji is a senior environmental soil scientist at MWRD. As co-PI, he will coordinate and assist sampling collection and extension activities at the MWRD research site (Task 3).

In this project, Dr. Zheng and Dr. Cooke are responsible for the quality assurance (QA) and quality control (QC) of research conducted in their laboratories (i.e., ISTC laboratory and WQL in the ABE) and fields. Dr. Zheng has over 20 years of experience in analytical chemistry and instrumentational operation. Dr. Cooke has extensive expertise in managing field-testing facilities. Dr. Guzman has research experience demonstrating competence in hydrology, contaminant transport, data science, and software development. He is responsible for data processes, analysis, and management and storage in this project. Laboratory technicians Sarmila Katuwal and Mahelet Maru are responsible for laboratory sample treatment and analyses in the ISTC laboratory and WQL in ABE, respectively. Ms. Lauren Lukins from Illinois Farm Bureau (IFB) as an outside external organization will assist extension and outreach activities (e.g., organizing field days). Ecosystem Exchange Services will provide cost-benefit analyses for the innovative technology as a third party with assistance of Drs. Cooke and Oladeji. A post-doc researcher, graduate student, and student helpers are being hired to implement laboratory and field experiments. PI and co-PIs are responsible for laboratory safety and training post-doc researcher and students working in the laboratories and fields. The organizational structure is shown in Figure 4.

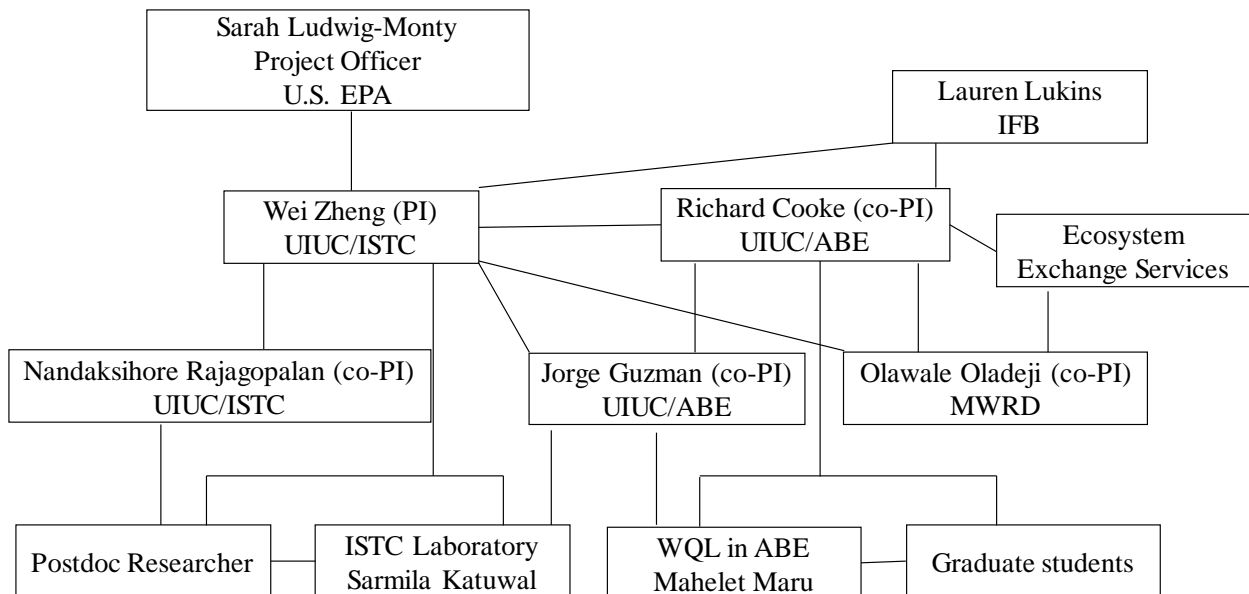


Figure 4. Project organization chart

A7. Quality Objectives and Criteria for Measurement Data

A7.1. Quality objectives

Objective 1 of the project is to create designer biochars by pyrolysis of biomass pre-treated with lime sludge and optimize the production conditions to generate the most efficient and cost-effective designer biochar to capture dissolved phosphorus and $\text{NH}_4\text{-N}$. Quality Objective 1 is to obtain accurate data and knowledge regarding the sorption kinetics and capacities of dissolved phosphorus and $\text{NH}_4\text{-N}$ on designer biochars.

Objective 2 of the project is to develop and demonstrate the B^2 nutrient treatment system to remove $\text{NO}_3\text{-N}$ and capture dissolved phosphorus, total phosphorus, and $\text{NH}_4\text{-N}$ from tile drainage water by conducting field experiments. Quality Objective 2 is to obtain accurate data and knowledge regarding the removal of nitrogen and phosphorus by the B^2 nutrient treatment system.

A7.2. Measurement performance criteria

This project aims to develop an innovative B^2 treatment to mitigate the excess nutrient loads to watershed from agricultural fields, thereby diminishing the occurrence of HABs. The primary measurement parameters in the project are $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, dissolved phosphorus, and total phosphorus. Their measurement quality criteria are shown in Table 2, including precision, accuracy, completeness, and method detection limits (MDLs).

Precision: It is the degree of agreement among repeated measurements of the same analyte under the same condition, indicating how constant and reproducible the field sampling or analytical procedures have been. Precision will be measured by analyzing results from field duplicate sampling for drainage water samples. Laboratory precision will be measured by analyzing results from duplicate laboratory samples. Comparing overall project precision and laboratory precision will help to identify sources of imprecision during the sampling and analysis of the samples. Field and laboratory precisions will be considered acceptable if the measurements fall within 30% and 10% relative percent difference (RPD) for duplicates, respectively (Table 2).

Accuracy: It is a measure of confidence in a measurement and will be determined quantitatively by analyzing matrix spiked samples for laboratory analyzed constituents. In this project, accuracy will be considered acceptable if the measurements fall within 15% percent difference (PD) based on the recovery of standards for all three targeted parameters (i.e., $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, dissolved phosphorus, and total phosphorus) (Table 2). Precision and accuracy of laboratory procedures are ensured by analyzing QC samples, including procedural/filter blanks, prepared standards, laboratory control samples, laboratory replicates, and field replicates, as applicable.

Completeness: It is expected that 100% of the samples collected and intended for analysis will be analyzed. However, a sample loss of <10% for the entire project will not compromise the objectives of the project.

Table 2: Targeted Parameters and Measurement Quality Criteria

Parameter	Units	MDLs	Field Precision	Laboratory Precision	Accuracy	Complete (%)
NH₄-N	mg/L	0.01	≤ 30% RPD for field duplicated	≤ 10% RPD for field duplicated	± 15% PD based on the recovery of standards	90
NO₃-N	mg/L	0.05				
Dissolved Phosphorus	mg/L	0.01				
Total Phosphorus	mg/L	0.01				

A8. Special Training Requirements/Certifications

In this project, nutrient measurements use routine laboratory analyses and data validation; therefore, specialized training is not required. Also, special certifications relevant to implementing this project are not required. The personnel who work in the laboratory are required to complete annual safety training (e.g., general laboratory training and chemical safety training), which is provided through the UIUC Division of Research Safety. All safety training certificates will be documented by the laboratory managers (Drs. Wei Zheng and Richard Cooke). In addition, a special COVID-19 safety training provided by the UIUC Division of Research Safety is required for all personnel during the pandemic.

A9. Environmental Concerns and Mitigation

The B² treatment system will be installed at the edges of fields, which will have less effect on the environment and crop fields during sampling. This project targets nutrient capture from drainage water. It does not have a hazardous solid waste generation. Any waste solutions, including used solvents generated in the laboratory, will be collected in waste bottles and then labeled in a proper manner. The UIUC Division of Research Safety will pick up and dispose of them.

A10. Documentation and Records

Documents and records are created and maintained according to the guidelines and requirements of ISTC laboratory and WQL in ABE. The ISTC laboratory is to conduct batch experiments to investigate the sorption capacities of different designer biochars for NH₄-N, dissolved phosphorus, and total phosphorus. The ISTC laboratory will maintain documents relevant to laboratory activities and data entry into the project files. The experimental procedures and raw data will be reported initially into laboratory notebooks and then transferred onto electronic files. The laboratory retention system includes notebooks, raw data, instrument reports, calculated data, and electronic documents. Summaries of NH₄-N, dissolved phosphorus, and total phosphorus analyses and quality control measures (laboratory duplicates, laboratory blanks, and laboratory media spikes) will be reported to the laboratory manager and PI (Dr. Wei Zheng). All laboratory

documents will be archived indefinitely at the ISTC laboratory and are available upon request.

WQL in ABE is to measure NO₃-N, NH₄-N, and dissolved phosphorus from drainage water samples collected from the B² treatment system in fields. In addition to the laboratory analytical documents, this laboratory will also maintain records related to field activities. The field records will contain at a minimum the following information, (1) project name, (2) date and time of sampling, (3) site name and location, (4) site condition, (5) personnel for sampling, and (6) pre- and post-field instrument performance checks where applicable. Field notes will be completed on-site as the time measurements occur. Field records will be recorded using a permanent pen; for any corrections needed, the error will be crossed out with a single line and the change initialed by the responsible person. All forms will be reviewed annually and updated as needed; the date of the most recent revision will be in the form's footnote. All field and laboratory documents will be archived indefinitely at WQL and are available on request. Co-PI (Dr. Richard Cooke) will be responsible for all documents and reports generated from WQL.

All hardcopy records such as laboratory notebooks and field notes are stored, secured, and protected in appropriate locations in both laboratories. All records and data stored in computers with electronic forms will be backed up weekly, monthly, and yearly by the laboratory technicians and managers. Periodically, backup copies of all electronic data are made on a portable hard drive to be kept off-site. All documents will be kept by PI and co-PIs for at least five years after the end of the project.

The QAPP will be reviewed annually and updated if there are significant changes. The document will be identified by title, date, and version number listed on the header of each page. All persons listed in the distribution list will receive updated copies.

B. Measurement / Data Acquisition

B1. Sampling Process Design (Experimental Design)

B1.1. Scheduled measurement activities and experimental design

There are two measurement activities in this project. One is to evaluate the sorption capacities of all produced biochars by conducting a series of batch experiments. In brief, 0.1 g of biochar will be weighed into a capped vessel followed by the addition of 25 mL of ammonium phosphate solutions of varying concentrations. All vessels will be shaken in a rotating tumbler at room temperature at 150 rpm. At appropriate time intervals, the vessels will be withdrawn, and the mixture will be filtered through 0.45 μm membrane filters. The filtrates will be immediately analyzed for the concentrations of $\text{NH}_4\text{-N}$ and dissolved phosphorus by spectrophotometric methods. This experiment will be conducted in the ISTC laboratory.

The other is to evaluate the B^2 nutrient treatment system through measuring the nutrient change in the tile drainage water. Water samples will be collected from influent (before the woodchip bioreactor), intermediate solution (after the woodchip bioreactor), and effluent (after biochar-sorption-channel) to determine the effectiveness of the bioreactor and designer biochars on the removal of $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, dissolved phosphorus, and total phosphorus. The total phosphorus will be analyzed at the ISTC laboratory. All other water parameters will be analyzed in WQL in ABE.

B1.2. Design rationale

The objectives of the project are to generate the most efficient and cost-effective designer biochars to capture phosphorus (dissolved and total phosphorus) and $\text{NH}_4\text{-N}$, and to demonstrate and scale up the B^2 nutrient treatment system to remove $\text{NO}_3\text{-N}$ and capture phosphorus and $\text{NH}_4\text{-N}$ from tile drainage water by conducting field experiments. In the batch experiment, adsorbed amounts for each biochar will be determined from the difference between the initial and filtrate concentrations of $\text{NH}_4\text{-N}$ and dissolved phosphorus. Accordingly, the most efficient and cost-effective designer biochar will be selected for the field study by evaluating and comparing their adsorption capacities and isotherms. In the field demonstration experiment, drainage influent, intermediate solution, and effluent will be collected to evaluate the removal efficiencies of the bioreactor for $\text{NO}_3\text{-N}$ and designer biochars for $\text{NH}_4\text{-N}$, dissolved phosphorus, and total phosphorus.

B1.3. Field sampling location and frequency

In this project, three field demonstrations will be conducted to evaluate the B^2 nutrient treatment system. In Year 1, a B^2 treatment system will be set up at the University of Illinois Dairy Farm (1-acre field) in Urbana, Illinois. This field study will be carried out for six consecutive months. Drainage water samples will be collected two times per week and additionally, within 24 hours of a rain event equaling or exceeding 0.5 inches. In Year 2, a scale-up B^2 treatment system will be conducted in an agricultural field (20-acre field) located on the MWRD's Nutrient Loss Reduction Research Site in Fulton County, Illinois. According to the previous hydrology data, this field demonstration study will be carried out for nine consecutive months since no drainage water flows

from July to September at the selected field site. Drainage water samples will be collected weekly and additionally, within 24 hours of a rain event equaling or exceeding 0.5 inches. In Year 3, multiple (up to 5) B² nutrient treatment systems will be established on a commercial corn production farm (100-acre field) in Champaign or Fulton County, Illinois. All water samples will be collected weekly or bi-weekly and additionally, within 24 hours of a rain event equaling or exceeding 0.5 inches. This field study will be carried out for nine consecutive months (July to September). Drainage samples will only be collected when there is flow.

B1.4. Classification of measurements as critical or non-critical

All measurements of NO₃-N, NH₄-N, dissolved phosphorus, and total phosphorus from laboratory and field experiments are considered critical due to their major targeted measurement parameters in the project. In the field study, the drainage water samples will be determined by a YSI multiparameter water quality meter on site for water temperature, dissolved oxygen, pH, and electrical conductivity. These parameters are considered non-critical (informational purposes only) since this project is not a monitoring study.

B2. Sampling Methods Requirements

B2.1. Field sampling collection, preparation, decontamination procedures

Drainage water will be collected directly by lowering a 50 mL sampling tube into the flowing stream of water with a custom-built sampling device shown in Figure 5. The tube will be filled and rinsed at least three times before keeping the fill. The collected water samples will be stored in the polyethylene bottles. Samples taken close to the university will be transported to WQL in ABE and frozen within two hours of collection. Samples from remote sites will be preserved with a drop (0.05 mL) of sulfuric acid within two hours of collection and shipped immediately to WQL in ABE. The measurement parameters, sample bottles, field preservation method and holding time are summarized in Table 3.

Table 3: Sample Collection, Handling, and Preservation Activities

Sample Type	Parameter Measured	Sample Container	Minimum Sample Size	Preservation Method/ Storage
Drainage water	Ammonium (NH ₄ -N)	Polyethylene bottles	25 mL	Pass sample through a glass fiber filter. Freeze the filtrate at -20 °C. Maximum holding time of 2 weeks
	Nitrate (NO ₃ -N)	Polyethylene bottles	25 mL	
	Dissolved Phosphorus	Polyethylene bottles	50 mL	
	Total Phosphorus	Polyethylene bottles	50 mL	



Figure 5. A custom-built sampling device for drainage water collection

The flow rate of tile drainage water will be measured at 15-minute intervals using a pressure transducer placed inside each structure. The flow rate is calculated from the depth of flow over a v-notch weir in the structure, based on calibration curves developed by co-PI (Dr. Richard Cooke) [55, 56].

B2.2. Sampling/measurement system failure response and corrective action process

From time to time, circumstances/conditions, e.g., broken or contaminated sample containers, may be identified prior to check-in or analysis, which, in turn, may dictate that a corrective action should be initiated. The corrective action process is summarized in Section C1.

B3. Sample Handling and Custody Requirements

B3.1. Field sampling preservation and holding times requirement

Samples generated from the batch sorption experiment in the laboratory will be analyzed immediately. Samples collected from the fields will be stored on ice in coolers and transported into the laboratory. Upon the laboratory, the samples will be immediately passed through a glass fiber filter except the samples used for total phosphorus analysis. All filtrates and nonfiltrates will be stored in a freezer at -20 °C. The holding times will be met to ensure the accuracy of the results (Table 3). The temperature of sample storage will be monitored routinely to verify that holding temperatures are met.

B3.2. Sampling custody requirement

All sample labels will be prepared in the laboratory prior to visiting the fields. Each sampling

bottle will be labeled with a unique identification number (i.e., Date-Location-Number). The bottles sent to the laboratory will be entered into WQL with their unique identification number. In addition, samples sent to the laboratory will also be accompanied by a copy of the relevant field sampling log and a chain of custody (COC) form. The COC forms will have the same identification number as the corresponding label on the sample container, ensuring the tracking of sample time and location. The COC forms will be signed and dated by the sampling staff.

B4. Analytical Methods

Samples generated from the batch sorption experiment will be analyzed in the ISTC laboratory. Total phosphorus in water samples collected from fields will also be analyzed in the the ISTC laboratory. The analyses of NH₄-N, dissolved phosphorus, and total phosphorus will be conducted according to standard methods outlined by the U.S. EPA [57] and the Standard Methods for Water and Wastewater [58] using an Agilent Cary 60 UV-Vis spectrophotometer. In addition to total phosphorus, water samples collected from the fields will be analyzed by WQL in ABE. The concentrations of NH₄-N, NO₃-N, and dissolved phosphorus are measured colorimetrically on an Astoria Analyzer based on their relevant USEPA methods. This instrument automates standard manual techniques for the analysis of nutrients. The preparation and analysis of water samples are described in Appendices A, B, and C. Table 4 summarizes the analytical methods and standard operating procedure (SOP) protocols performed by the ISTC laboratory and WQL.

Table 4. Methods for Nutrient Analyses to be Conducted by ISTC Laboratory and WQL

	Parameter	Units	Expected Range*	Methods and Analytical SOP Protocols
ISTC Laboratory	NH ₄ -N	mg/L	0.1~10	U.S. EPA Method for Chemical Analysis of Water and Waste [57] and Standard Methods for Water and Wastewater [58]
	Dissolved Phosphorus	mg/L	0.01~2.0	
	Total Phosphorus	mg/L	0.01~2.0	
WQL	NH ₄ -N	mg/L	0.01~2.0	Ammonia Nitrogen A023 (please see Appendices A)
	NO ₃ -N	mg/L	0.05~10	Nitrate + Nitrite A173 (please see Appendices B)
	Dissolved Phosphorus	mg/L	0.01~1.0	Ortho-Phosphate A203 (please see Appendices C)

* If the sample exceeds the detection range, an appropriate dilution is performed, and the test is repeated.

The calibration procedure for laboratory instruments is documented in section B7. All laboratory calibration records will be reviewed by analysts and maintained in the laboratory document retention systems. Both laboratory managers and PI will examine analytical results. They are also

responsible for starting a corrective action (including re-extraction, reanalysis, and data qualifier) when a failure in the analytical system occurs.

B5. Quality Control

For both participating laboratories (ISTC laboratory and WQL in ABE), the laboratory managers and PI must ensure and document that the method performance meets the data quality objectives and criteria requirements identified in A7. QC samples will be run with every analytical batch of 20 samples or fewer. In this project, the QC samples typically used for evaluation of laboratory and field sampling performance are as follows:

Method blanks: A sample of deionized water free from the analytes of interest will be processed simultaneously with and under the same conditions as samples through all analytical procedures. The method blank aims to demonstrate that the analytical system is free of target analytes and interferences.

Field blanks: A sample of deionized water free from the analytes of interest will be processed simultaneously with and under the same conditions as samples through the sampling procedure, then analyzed much like an ordinary field sample. Field blanks check for contamination from the sample bottles and field sampling techniques.

Laboratory control sample: A sample matrix, free from the analytes of interest and interferences, spiked with verified known amounts of analytes will be used to establish intra-laboratory or analyst specific precision and bias and to assess the performance of the entire measurement process.

Standard reference: Standard materials purchased or created by laboratory standards will be used as internal reference samples to track performance across batches and calibrate instruments.

Instrument duplicate: The samples or standards analyzed twice by an instrument from the same container to measure the instrumental precision.

Laboratory Dduplicate: A second aliquot of a sample taken as the first aliquot under laboratory conditions and processed and analyzed independently.

Field duplicates: Two aliquots of water taken from one field sample and filtered in the field as two separate samples, resulting in two filters or two filtrates.

Internal standards: Analytes introduced after the last sample-processing step prior to analysis, to measure and correct for losses and errors introduced during analysis, with recoveries and corrections to reported values generally reported for each sample individually.

In addition, the field QC also includes replicate readings for *in-situ* measurements (e.g., pH, conductivity, and temperature) using a YSI meter. Acceptance QC criteria for targeted parameters are specified in the section of A7 (Table 2). If the QC samples do not meet acceptance criteria, the data will be checked with the laboratory for transcription errors, flagged as questionable, or censored. Corrective actions will be taken (e.g., re-training, repeat sampling when feasible, rerun samples, and recalibration of instruments or using maintenance service) to assure acceptable results. All QC results will be recorded in the project database.

B6. Instrument/Equipment Testing, Inspection, and Maintenance Requirements

The field sampler (Figure 5) will be inspected prior to each sampling event and will be maintained throughout the sampling season and prior to storage during the off-season. The laboratory instrument or equipment (e.g., Astoria autoanalyzer, spectrophotometer, analytical balances, and electronic pipette) used for nutrient analyses will be calibrated and maintained by laboratory staff according to their respective SOPs or the manufacturer's specifications. All instrument or equipment will be checked or inspected before each use. Table 5 summarizes the inspection and QC checks for the main instruments used in this project. An instrument logbook will be maintained to document periodic maintenance of major equipment.

Table 5: Quality Control Checks, Inspection, and Maintenance for Instruments

Instruments	QC Check	Frequency	Data Summary	Acceptance Criteria	Action if values are unacceptable
Astoria Analyzer	Calibration with standards of targeted analytes	Before each use	Plot linear regression	Linear response, $R^2 > 0.99$	Repeat calibration or perform maintenance
Sartorius Analytical Balances	Record readings for NIST traceable standard weights	Quarterly	Calculate accuracy	Greater than stated QC	Reweigh samples on another balance. Arrange to have balance serviced
Agilent Cary 60 Spectrophotometer	Calibration with standards of targeted analytes	Before each use	Plot linear regression	Linear response, $R^2 > 0.99$	Repeat calibration or perform maintenance
Electronic Pipette	Determine mass of dispensed water volume	Monthly	Single measurement	Within +/- 1% of expected volume	Clean, adjust, replace pipette. Return defective pipettes to vendor for service
YSI Multiparameter Water Quality Meter	Calibrated using standards	Before and after use	Multiple measurements	Within +/- 10% of the expected values	Clean probe, replace membrane or service as necessary and recalibrate

B7. Instrument Calibration and Frequency

All laboratory instruments involved in targeted parameter analyses shall be inspected, maintained, calibrated (as applicable), and tested prior to use. Laboratory instruments are calibrated, standardized, and maintained the following procedures detailed in laboratory SOPs. Calibration procedures and frequency for laboratory and field instruments are summarized in Table 6. All laboratory calibration records will be reviewed by the laboratory managers and maintained in laboratory notebooks.

Table 6: Instrument Calibration and Frequency

Instrument	Calibration Procedure	Frequency
Astoria Analyzer	Calibrated by a service technician during annual maintenance	Yearly service Check before each use
Sartorius Analytical Balances	Calibrated by a service technician during annual maintenance	Yearly service Check before each use
Agilent Cary 60 Spectrophotometer	Calibrated by a service technician during annual maintenance	Yearly service Check before each use
Electronic Pipette	Calibrated by a service technician during annual maintenance	Yearly service Check before each use
YSI Multiparameter Water Quality Meter	Calibrated using standards	Before and after each use

The Astoria analyzer and spectrophotometer are the main analytical instruments to measure NO₃-N, NH₄-N, and dissolved phosphorus in this project. Both analytical instruments will be calibrated at the beginning of each assay by analysis of at least six dilutions of stock standards for each analyte. The calibration curve is acceptable if it has an R^2 of 0.99 or greater for all targeted analytes. If analytical instrumentation fails to meet the performance requirements, the instruments will be checked according to their SOPs and recalibrated. If the instrument does not meet specifications again, it will be serviced and retested until performance criteria are achieved. The maintenance will be entered in the instrument log. The YSI meter will be calibrated before field-use, and calibration will be checked after each sampling event to ensure that it has remained calibrated throughout use.

B8. Inspection/Acceptance Requirements for Supplies and Consumables

All supplies and consumables are ordered and, when received, checked/verified by the laboratory staff. All reagents and chemicals should be analytical reagent grade or higher. Reference standards (>99%) are purchased according to the requirements of the respective analysis SOP. Laboratory staff shall log in all chemicals to the appropriate logbook and dated upon receipt. Also, all supplies, chemicals, and standards shall be stored appropriately following manufacturer recommendations.

Chemicals and reference standards shall be discarded upon expiration date or if there is evidence that the material is degraded or damaged. All deionized water used is polished with a MiliQ water polishing system to a resistivity of no less than 18 M Ω -cm.

Sample bottles for drainage water sampling are purchased from the same vendor throughout the project. All sample bottles are inspected visually by laboratory staff before use and must be clean and free of cracks; sample bottles with preservative are inspected visually for the presence of preservative. Sample bottles must be correctly labeled.

Appropriate corrective actions will be taken for supplies and consumables not meeting acceptance criteria, e.g., replacement and returning to the vendor.

B9. Data Acquisition Requirements (Non-direct Measurements)

Tile drainage location, depth, and water flow obtained from previous studies are pre-documented for this project as non-direct measurement data. These existing data will provide some qualitative information to design and install the B² treatment systems and manage sampling time and frequency.

B10. Data Management

B10.1. Data recording

Data management activities include data collection, processing, and analysis that are essential components of the project. In this project, data will be collected from both laboratory and field experiments. Data collected from the laboratory are experimental results that will essentially support comparative analysis of nutrient sorption on designer biochars. For the field data, time series of drainage water concentrations will serve to evaluate the removal of NO₃-N in the bioreactors and adsorption of dissolved phosphorus, total phosphorus, and NH₄-N by the biochar-sorption-channel system. The project will generate and use different types of data, including:

- Quantitative data on dissolved phosphorus, total phosphorus, and NH₄-N by designer biochars in the laboratory.
- Quantitative data on NO₃-N removal by woodchip bioreactors in the fields.
- Quantitative data on dissolved phosphorus, total phosphorus, and NH₄-N removal by the biochar-sorption-channel systems in the fields.
- Quantitative data on water quality and tile drain flow in the field studies.
- Images data regarding biochar characterization.
- Fieldwork photos and/or videos.

The laboratory experimental data will either be manually recorded in laboratory notebooks and field spreadsheets, or automatically entered from instrument data systems. All personnel is required to maintain a hard copy (e.g., notebooks) or electronic files for primary data recording.

Statistical treatment of experimental data will be performed using standard analytical techniques (e.g., computation of mean and standard deviation). The laboratory manager and PI or co-PIs will be responsible for verifying the accuracy of the data and for deciding whether the data meet the measurement quality objectives. Any data that do not meet the criteria for quality, accuracy, and precision will be discarded, and the corresponding experiments will be repeated.

B10.2. Location of public accessibility of data

The laboratory and field experimental data will drive preliminary screening before they are made available to the public. Reports and documents will be produced along with analysis figures and data tables. Where appropriate, published papers in peer-reviewed journals, Illinois Digital Environment for Access to Learning and Scholarship (IDEALS), and the UIUC digital repository will disseminate and preserve documents. The final data products will be published at the Illinois Data Bank (<https://databank.illinois.edu/>) maintained by the UIUC Library for public accessibility.

B10.3. Standards for format and content

In most cases, data generated by a particular instrument is stored in a proprietary format determined by the manufacturer. The data will be parsed and stored in the database. If possible, the experimental data will be converted to readily useable formats such as ASCII, Excel, or PDF for further manipulation and archiving. Images will be converted to PNG or TIFF formats. The data and metadata about the instruments/sensors will be extracted and managed in the database. The metadata describing the data will include observation/measurement specifications (for example, units, time zone, etc.), PI/co-PI name, project name, graduate student/technician name, and laboratory notebook volume and page number. Spreadsheets and other digitally stored data will be linked to laboratory notebooks via file names. The project will have a dedicated folder on the laboratory computer, where the digital data will be stored and routinely backed up. Physical samples such as water and soil will be stored using appropriate laboratory protocols with labels containing PI name, graduate student name, and date.

B10.4. Policies for data sharing and public access

Access to data and metadata will be made available to researchers and public entities following the publication of the analytical work. Full data sets will be provided in the supporting information of our publications with a summary of critical results in the article's main text where possible. If this is not possible, links to public repositories, such as the farm management software, IDEALS, and Illinois Data Bank, will be provided in the publications. After the research publication, the data and source code will be made available to the public as open data/open source. Derivative educational products will also be shared freely by posting to the applicants' website. Any sharing data should be consistent with all applicable laws, regulations, and U.S. EPA guidelines and policies. Any data related to confidentiality, personal privacy, personally identifiable information, and U.S. national, homeland, and economic security will be handled with proper diligence to avoid public release.

B10.5. Plan for data storage, archiving, and preservation

All electronic data, including instrument outputs, spreadsheets, pictures, and modeling data, will be stored in multiple places, including a local computer hard drive and a cloud storage/synchronization service (e.g., box) that will also enable easy data access and sharing among the project team. Periodic backup of data on an isolated external hard drive will also be performed to provide additional long-term data protection. The experimental data, including the laboratory notebooks, will be kept in the laboratories of PI and co-PIs for at least five years after the end of the project. Physical samples generated during experiments (water, biomass, and lime sludge) will be stored under appropriate conditions.

B10.6. Data accessibility and preservation

Publication in peer-reviewed journals and presentations at scientific meetings will be the primary means of providing access to the research products including all laboratory and computational procedures, results, and analysis of those results. All sample preparation procedures, characterization, and testing methods will be fully described in publications to enable outside replication of findings. Charts, figures, and images will be provided in article texts, with necessary raw data in supplementary information sections. Data will also be disseminated in annual reports to U.S. EPA and presentations delivered at national and/or international conferences. Copies of primary data pertaining to published work will be made available upon request. Laboratory notebooks and reports remain property of the research group, but relevant portions will be shared through presentations and publications.

B10.7. Roles and responsibilities

The PI and Co-PIs have the primary responsibility for implementing the data management plan (DMP). The PI will ensure that all workers on this project are aware of the DMP and strictly follow all the protocols outlined in this document. Suppose the key personnel (including post-doc scientists and students) leave the project. The PI and co-PIs will take all project data (including laboratory notebook and reports) and protect any confidential data. The PI has the full responsibility to manage and disseminate all data generated in the project.

C. Assessment/Oversight

C1. Assessments and Response Actions

This project aims to develop and scale up an innovative B² treatment system (Figure 1) to effectively capture nutrients from subsurface drainage water and recycle nutrient-captured biochars as a slow-release fertilizer, and keep nutrients in a closed agricultural loop. The performance objectives, proposed activities, and expected success criteria for the project assessment are shown in Table 7.

Table 7. Objectives, Proposed Activities, and Expected Success Criteria

Objectives	Activities	Criteria
Create designer biochars and optimize the production conditions to generate the most efficient and cost-effective designer biochar to capture phosphorus and NH ₄ -N.	Produce designer biochars under different conditions. Conduct batch experiments to evaluate all produced biochars. Manufacture biochar pellets. Develop web pages about the project.	Finalize the production conditions to manufacture the most efficient and cost-effective designer biochar for the field study.
Develop an innovative B ² nutrient treatment system by integrating refillable biochar-sorption-channels with woodchip bioreactors.	Design and develop a B ² system and demonstrate it in a field trial. Update webpages on the progress of the project.	Set up a B ² system in the research fields to successfully capture nutrients from drainage water.
Scale up the B ² nutrient treatment system to remove NO ₃ -N and capture phosphorus and NH ₄ -N from tile drainage water.	Design and develop a scale-up B ² system. Conduct a field study to demonstrate the scale-up B ² system. Update webpages on the progress of the project.	Set up a scale-up B ² system in the research fields to successfully capture nutrients from drainage water.
Evaluate the developed B ² nutrient treatment system by conducting a scale-up field study.	Execute field demonstration study on a commercial farm. Update webpages on the progress of the project.	Establish five B ² systems in the crop fields to capture nutrients from drainage water successfully.
Recover nutrients by applying nutrient-captured biochars as a slow-release fertilizer to improve crop yields.	Conduct a field trial for nutrient-captured biochar as a fertilizer Update webpages on the progress of the project.	Demonstrate the potential of nutrient-captured biochar as a fertilizer.

The project assessment will be performed quarterly by the PI and co-PIs to review the progress of the project. In addition to the project assessment, other assessment activities, including laboratory audits, are summarized in Table 8. When the project is initiated, both laboratory managers will

perform an initial performance audit to determine if each laboratory can meet the requirements of the QAPP and assist the laboratory where needed. The laboratory managers will review every data file submitted as part of these audits and ensure that QC issues will be addressed as soon as they are detected. Results will be reviewed with laboratory staff and corrective action will be recommended and implemented, where necessary. If data quality issues are identified, a preliminary meeting will be held between the laboratory managers and laboratory staff to discuss possible solutions. If necessary, a corrective action plan will be developed. Examples of situations requiring initiation of the corrective action process include mishandling of a sample or its documentation, deficiencies discovered during an internal audit, or use of unapproved modifications to an analytical method. After the required corrective action is taken, the problem and its resolution will be documented and reviewed by the QA manager. All information concerning response actions will be maintained in the project files by laboratory managers and will be noted in any reporting that includes affected data.

Table 8. Planned Project Assessment

Assessment Type	Frequency	Internal/ External	Organization	Person(s) Responsible
Project progress review	Quarterly	Internal	UIUC/ISTC, ABE, and MWRD	PI and co-PIs
ISTC laboratory systems	Annually	Internal	UIUC/ISTC	Wei Zheng
WQL technical systems	Annually	Internal	UIUC/ABE	Richard Cooke
Field sampling system	Annually	Internal	UIUC/ABE	Richard Cooke
Data quality assessment	Annually	Internal	UIUC/ABE	Jorge Guzman
QAPP	Annually	Internal	UIUC/ISTC	Lee Green
Report review	Annually	External	USEPA	Sarah Ludwig-Monty

C2. Reports to Management

Information concerning any proposed activities and research results will be reported quarterly to the supervisors (i.e., the relevant co-PIs) and PI as a quarterly report. The PI and co-PIs will be responsible for compiling all results and submitting annual progress reports and a final report to the US EPA project officer. In addition, the QC reports including raw QC data and QC data and summary, summary of major/critical issues encountered and their resolution, and reconciliation of project data with project quality objectives will be reported to the QA managers and PI annually. The QA management report plan is summarized in Table 9.

Table 9. QA Management Report

Type of Report	Delivery Frequency	Person(s) Responsible	Report Recipient
Research results	Quarterly	Staff involved in the project	PI and co-PIs
Annual progress reports and final report	Annually, completion of the project	PI and co-PIs	US EPA project officer, general public, and stakeholders
QC	Annually	Laboratory managers	QA manager and PI

D. Data Validation and Usability

D1. Data Review, Verification, and Validation

All data will undergo review and evaluation to ensure that the data conform to quality objectives and criteria specified in this QAPP (the section of A7). Data will be evaluated as meeting or failing quality criteria by the laboratory staff and then reviewed by the laboratory managers. Before submitting data, the laboratory staff will perform a check of all of the records and field sheets or COC sheets they received from sampling staff (e.g., sampling equipment, sampler's initials, time of collection, preservation methods, and/or time of transfer). The laboratory managers will recheck 10%. The QA manager may review all checks. Data will be submitted to the PI and relevant co-PIs in electronic form. After data are submitted, they will be documented in the project files. PI or co-PIs will review the data set for completeness (e.g., correct numbers of samples and analyses, appropriate QC sample data included) and accuracy (e.g., in sample IDs), and spot-check for consistency with hardcopy results reported by the laboratory. In addition, the PI and co-PIs will also verify that appropriate sampling and analytical methods have been used, instruments have been functioning correctly, samples have been analyzed within holding times, and that measurements have been within the calibration ranges.

Data that are incomplete, inaccurate, or failing quality criteria without appropriate explanation will be referred back to the laboratory for correction or clarification. The PI and co-PIs will discuss data failing quality criteria with laboratory staff to determine corrective actions and whether the samples need to be rerun. If problems cannot be readily corrected (e.g., insufficient sample, irremovable interferences, or blank contamination), results outside the quality criteria will be flagged to alert data users to uncertainties in quantitation.

D2. Verification and Validation Methods

Data verification ensures that the reported results reflect what was done and documents that the data fulfill applicable requirements. Data validation is to identify and evaluate the impact of any technical non-compliance or quality control non-conformances on the complete data set. Verification and validation for all data generated from laboratory and fields will be the combined responsibility of the PI (Dr. Wei Zheng) and two co-PIs (Drs. Richard Cooke and Jorge Guzman). To verify and validate the data derived from laboratory and field studies, they will conduct the initial verification and validation checks and generate the initial data package, including field sheets, raw data and data summaries, COC forms, and research results.

The methodology used to verify and validate field data will include: checking field procedures and sampling locations; evaluating the field documents for consistency; ensuring that holding times are met; ensuring that field measurement equipment is calibrated correctly; checking for transcription errors and outliers; and comparing the results with quality criteria. The methodology used to verify and validate analytical data from the laboratory will include: examining appropriate analytical methods that have been used in the project; checking QC that has been identified in the QAPP (e.g., MDLs, blanks, replicates, and relative percent difference); ensuring analytical instruments that have been operated under acceptable performance conditions; and comparing the

analytical data with quality criteria and ensuring that the analysis has been within the calibration ranges. If verification and validation checks identify a corrective action situation, it is the PI's responsibility to approve the implementation of corrective action, including re-sampling and/or re-analyzing samples, during data assessment. The PI will document all corrective actions of this type.

D3. Reconciliation with User Requirements

Data derived from the laboratory or field are assessed to determine usability and whether the data support their intended use. As indicated in section D2 above, the PI and co-PIs will review the data to determine if the quality criteria have been met. If the quality criteria are not met, the cause of the failure will be evaluated, and the following actions may be applied: a review of the system in question; re-sampling; schedule replicate sampling of the site during the next sampling event; rejection of the data and exclusion from the report; or, if other measures fail, reconsideration of quality criteria. Any modification to the quality objectives and criteria, the revision QAPP will be submitted to the US EPA for review. Deviations from SOPs, failure to meet quality criteria, questionable data, and limitations using the data will be noted in the QC sheet for each data package. Limitations to the use of the data will be noted in the project progress reports and final report. Results from this study and their utility for addressing management questions may also inform decision-makers about any future studies and any modifications that may be required. In addition, the product (i.e., designer biochar) from this project will be promoted for its application in the environment and agriculture through outreach and extension activities.

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