

FINAL REPORT

Development, Evaluation, and Technology Transfer of BMPs for Optimizing Removal of PAHs, PCBs, PFAS, and Metals from Stormwater at DoD Sites

Staci Massey Simonich
Richard Hilliard
Bethany Parker
Oregon State University

December 2022

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REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 08-06-2022		2. REPORT TYPE SERDP Final Report		3. DATES COVERED (From - To) 7/27/2018 - 12/31/2022	
4. TITLE AND SUBTITLE Development, Evaluation, and Technology Transfer of BMPs for Optimizing Removal of PAHs, PCBs, PFAS, and Metals from Stormwater at DoD Sites				5a. CONTRACT NUMBER 18-C-0074	
				5b. GRANT NUMBER W912HQ18C0074	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Staci Massey Simonich (Department of Environmental and Molecular Toxicology), Jennifer Field (Department of Environmental and Molecular Toxicology), Meghna Babbar-Sebens (School of Civil and Construction Engineering), Tyler Radniecki (School of Chemical, Biological, and Environmental Engineering), Greg Wilson (College of Earth, Ocean & Atmospheric Sciences)				5d. PROJECT NUMBER ER18-1230	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
				8. PERFORMING ORGANIZATION REPORT NUMBER ER18-1230	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Oregon State University (see individual colleges as above) 1500 SW JEFFERSON ST CORVALLIS, OR 97331-8655				10. SPONSOR/MONITOR'S ACRONYM(S) SERDP	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) ER18-1230	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Strategic Environmental Research and Development Program 4800 Mark Center Drive, Suite 16F16 Alexandria, VA 22350-3605					
12. DISTRIBUTION / AVAILABILITY STATEMENT DISTRIBUTION STATEMENT A. Approved for public release: distribution unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT SERDP project number ER18-1230 was designed to create and evaluate a novel bioswale design, utilizing a treatment train of sand, plants, and sorbents, for the removal of polycyclic aromatic hydrocarbons (PAHs) (and their toxic degradation products), polychlorinated biphenyls (PCBs), per- and poly-fluoro-alkyl substances (PFASs), and heavy metals (Cu ²⁺ and Zn ²⁺) from contaminated stormwater at relevant DoD sites. Of the five sorbents tested (bioswale soil, granulated activated carbon, Biochar Basic™, EarthLite™ and RemBind®), Biochar Basic™ demonstrated superior removal of heavy metals and RemBind® demonstrated superior removal of PFASs under clean synthetic stormwater conditions. Under real stormwater conditions, all supports demonstrated significant decreases in removal capabilities and suggested that a pretreatment stage may be necessary. Additional experiments were conducted to determine which water quality constituents were key to remove during pretreatment. Ten plant species located in our research bioswale (both grasses and broad leafed) were evaluated for their ability to remove heavy metals. In general, broad-leafed plants showed superior Zn ²⁺ removal (especially checker mallow, yarrow, and salal) while grasses showed superior Cu ²⁺ removal (especially slough sedge and dense sedge). A pilot-scale implementation utilizing sorbent column studies generated new protocols to characterize the capture and movement of sediments through the bioswale using silt sized (~20 mm diameter) fluorescent-magnetic tracers and fluorescent probes. These findings were integrated in the stormwater management model (SWMM) for the design of a pilot treatment train and further implementation of SWMM model.					
15. SUBJECT TERMS stormwater, PAH, PFAS, heavy metals, sorbent, bioswale, low infrastructure design, magnetic tracer, fluorescent probe, SWMM model					
16. SECURITY CLASSIFICATION OF: Unclassified			17. LIMITATION OF ABSTRACT UNCLASS	18. NUMBER OF PAGES 121	19a. NAME OF RESPONSIBLE PERSON Staci Simonich
a. REPORT UNCLASS	b. ABSTRACT UNCLASS	c. THIS PAGE UNCLASS			19b. TELEPHONE NUMBER (include area code) 541-207-7901

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Abbreviations and Acronyms

ACN	acetonitrile
AEC	Anion exchange capacity
AFFF	Aqueous film forming foam
BCF	bioconcentration factors
CEC	Cation exchange capacity
CO ₂	carbon dioxide
DCM	dichloromethane
DOC	dissolved organic carbon
EMC	event mean concentrations
FOSA	Perfluorooctane sulfonamide
FtB	Fluorotelomer betaines
FTCA	Fluorotelomer carboxylates
FTSaB	Fluorotelomer sulfonamido betaine
FTAoS	Fluorotelomer thioamido sulfonate
FTSAOAoS	Fuorotelomer sulfoxide amido sulfonate
FTSAO ₂ AoS	Fluorotelomer sulfone amido sulfonate
FTTHN	Fluorotelomer thio hydroxy ammonium
FTTPA	Fluorotelomer thioether propanyl alaninate
FTSaAm	Fluorotelomer sulfonamide amine
FTSA	Fluorotelomer sulfonate
FTUCA	Fluorotelomer unsaturated carboxylate
GC	Gas chromatography
HCl	Hydrochloric acid
HPLC	High performance liquid chromatography
ICP	Inductively coupled plasma
<i>K_d</i>	Soil:water partition coefficient
<i>K_f</i>	Freundlich sorption coefficient
<i>K_{oc}</i>	Organic carbon:water partition coefficient
LID	Low Impact Development
LC-MS/MS	Liquid chromatography tandem mass spectrometry
MeOH	methanol
MilSpec	Military specification
MS	Mass Spectrometry
N ₂	Nitrogen
NaOH	sodium hydroxide
NH ₄ OH	Ammonium hydroxide
PAH	polyaromatic hydrocarbons
pK _a	Acid dissociation constant
PFASs	Perfluoroalkyl substances
PFBA	Perfluorobutanoate
PFBS	Perfluorobutane sulfonate
PFCA	Perfluorinated carboxylate
PFDA	Perfluorodecanoate
PFDoA	Perfluorododecanoate

PFDS	Perfluorodecane sulfonate
PFEtS	Perfluoroethane sulfonate
PFHpA	Perfluoroheptanoate
PFHpS	Perfluoroheptane sulfonate
PFHxA	Perfluorohexanoate
PFHxS	Perfluorohexane sulfonate
PFHxSA	Perfluorohexane sulfonamide
PFNA	Perfluorononanoate
PFNS	Perfluorononane sulfonate
PFOA	Perfluorooctanoate
PFOS	Perfluorooctane sulfonate
PFPeA	Perfluoropentanoate
PFPeS	Perfluoropentane sulfonate
PFPrS	Perfluoropropane sulfonate
PFSA	Perfluoroalkyl sulfonate
PFSaAm	Perfluoroalkyl sulfonamido amine
PFSaAmA	Perfluoroalkyl sulfonamide amino carboxylate
PFTTrA	Perfluorotridecanoate
PFTeA	Perfluorotetradecanoate
PFUnA	Perfluoroundecanoate
QTOF	Quadrupole time of flight
SPE	solid phase extraction
ΣPFAS	Sum-Total PFAS
TCE	Trichloroethene
TDS	total dissolved solids
TOP	Total oxidizable precursor
TQD	Tandem / Triple quadrupole detector
TSS	total suspended solids

Acknowledgements

The research described in this final report was supported by the US Department of Defense, through the strategic environmental research and development program (SERDP) Dr. Andrea Leeson and other SERDP staff are knowledge for their assistance and support.

Abstract

SERDP project number ER18-1230 was designed to create and evaluate a novel bioswale design, utilizing a treatment train of sand, plants, and sorbents, for the removal of polycyclic aromatic hydrocarbons (PAHs) (and their toxic degradation products), polychlorinated biphenyls (PCBs), per- and poly-fluoro-alkyl substances (PFASs), and heavy metals (Cu^{2+} and Zn^{2+}) from contaminated stormwater at relevant DoD sites. Of the five sorbents tested (bioswale soil, granulated activated carbon, Biochar Basic™, EarthLite™ and RemBind®), Biochar Basic™ demonstrated superior removal of heavy metals and RemBind® demonstrated superior removal of PFASs under clean synthetic stormwater conditions. Under real stormwater conditions, all supports demonstrated significant decreases in removal capabilities and suggested that a pretreatment stage may be necessary. Additional experiments were conducted to determine which water quality constituents were key to remove during pretreatment. Ten plant species located in our research bioswale (both grasses and broad leafed) were evaluated for their ability to remove heavy metals. In general, broad-leafed plants showed superior Zn^{2+} removal (especially checker mallow, yarrow, and salal) while grasses showed superior Cu^{2+} removal (especially slough sedge and dense sedge). A pilot-scale implementation utilizing sorbent column studies generated new protocols to characterize the capture and movement of sediments through the bioswale using silt sized (~20 mm diameter) fluorescent-magnetic tracers and fluorescent probes. These findings were integrated in the stormwater management model (SWMM) for the design of a pilot treatment train and further implementation of SWMM model.

Executive Summary

Introduction

The overall goals of this project were to: (1) develop innovative stormwater control and treatment technologies that improve stormwater management, prevent sediment recontamination, and add to the existing water supply, and to (2) develop watershed modeling of new stormwater control processes that focus on sediment-related contaminants to provide information on the efficiency needed and the number of systems deployed to prevent sediment recontamination and increase stormwater harvesting.

Objectives

To achieve these overall goals, the four specific tasks of this SERDP project were as follows:

Objective 1: Improve lab-scale mechanistic understanding of the fate and transport of PAHs, PCBs, PFASs, Cu^{2+} , and Zn^{2+} through commercially available stormwater sorbents (bioswale soil, GAC, Biochar Basic™, EarthLite™, and RemBind®). This Task was further extended past the original proposal and budget to accommodate SERDP requests for including stormwater from DOD site Willow Grove and additional sorbent analysis (Calgon). This significantly changed the original timing and progress for further aspects of the project as these were not originally part of the scope of this work.

Objective 2: Improve lab-scale, mechanistic understanding the fate and transport of heavy metals, PAHs, PCBs, and PFASs through vegetated bioswales containing native grasses, broad-leaf plants, and their associated microbial communities. This further included microbiome sequencing and analysis to determine performance markers for stormwater and plant/microbiome dependencies.

Objective 3: Conduct field scale testing to investigate the fate and transport of PAHs, PCBs, PFAS, heavy metals, nutrients, total solids, and organic carbon in three types of Green Infrastructure BMPs, for multiple storm events. The primary goal of this objective will be to characterize the fate and transport of PFAS-associated particulates in the field and use the results of the lab-scale studies (from Objectives 1 and 2) to design, deploy and evaluate a novel treatment train at the field-scale, under a variety of storm intensities and environmental conditions.

Objective 4: Develop a new module for improving the simulation of plant-water-soil interactions for standard water quality parameters, and sediment-associated PAHs, PCBs, and PFAS in the USEPA SWMM model, and validate the improved model for multiple storm events using the field experiment data collected in Task 3.

This Final Report for SERDP ER18-1230 describes the research conducted to complete all Tasks and details of specific subtasks. Further progress about continuing and future progress towards aspects of Task 3 (field-scale studies) and 4 (modeling) are further noted.

Technical Approach

Task 1 utilized lab-scale batch isotherm and column experiments to characterize the removal of PAHs, PCBs, PFASs, Cu^{2+} , and Zn^{2+} by commercially available sorbents. Additionally, the column studies characterized the potential desorption of contaminants during periods of interrupted hydraulic loading. The sorbents tested included bioswale soil (25% mint compost, 25% municipal compost, and 50% native clay soil), granulated activated carbon, Biochar Basic™ (sourced from Douglas fir), EarthLite™ stormwater filter media (composite of hazelnut shell biochar, expanded shale, compost, and oyster shells), and RemBind® media (mixture of activated carbon, aluminum hydroxide, and kaolin clay). This Task was further extended past the original proposal and budget to accommodate SERDP requests for including stormwater from DOD site Willow Grove and additional sorbent analysis (Calgon).

In Task 2, treatment of real stormwater by 10 native and regional plants was investigated in a series of greenhouse experiments. The primary goal of Task 2.1 is to screen the ability of ten different bioswale plants, five grasses and five broad-leafed plants (see

Table 1 in Materials and Methods: Task 2), for their ability to remove heavy metals (Cu^{2+} and Zn^{2+}), PAHs, PCBs, and five model PFASs (PFBA, PFOA, PFHxS, PFOS, and FtSaB) from stormwater collected from our bioswale research facility. Plant-free mesocosms (soil only) were tested as negative controls. The plants represent a variety of root structures, leaf structures, growth rates, and nutrient requirements and are currently in use at our pilot-scale research bioswale facility (Livingston, 2015). All experiments were conducted in lab-scale mesocosms under greenhouse conditions (70 °F set point, 60-85 °F range, natural lighting). All plants and plant-free controls were tested in sextuplet 2.4 L mesocosms. Each mesocosm contained 2.2 kg of modified bioswale soil (50% sand (ASTM C-33 spec), 25% native clay soil, 12.5% mint compost, and 12.5% municipal compost). All mesocosms were irrigated with collected stormwater until fully saturated. The mesocosms remained saturated for 5 h before being drained. Irrigation occurred once per week for 10 weeks. Influent and effluent contaminant concentrations were quantified for each irrigation event. Task 2.2 was halted.

In Task 3, a set of field investigations were performed. A multi-stage treatment train intended to be used in a Low Impact Development (LID) model for on-side stormwater intake and remediation system was installed. This system intended to: characterize transport of sediment-associated PFAS compounds in LID using sediment tracer studies; temporally characterize plant stress in bioretention cells during wet and dry periods in the field, assess hydrologic performance of treatment train over multiple storms, and assess performance of contaminant treatment within the treatment train over multiple storms. Installation further included tracer studies to characterize spatial transport of PFAS-associated sediments, and design-build-evaluation of novel treatment train for passive treatment of sediments, nutrients, heavy metals, and PAHs.

Task 4 focused on field data collection for evaluation of treatment train and calibration and validation of Storm Water Management Model (SWMM) for simulation of treatment train hydrology and fate and transport processes. Data from multiple storm events and prior tasks will be assessed and assembled to simulate and address fate and transport based on pump controlled inflows for 24 hour durations. Current SWMM version five (SWMM5) includes options for: Constant percent Removal, Constant percent co-removal, Concentration dependent removal, Nth Order Kinetics, K-C* first order modeling, and Gravity Settling. Improvement in further simulation of interactions between plants, water, contaminants, microbes and microecologies, and soil was investigated. Mechanistic equations in existing phytoremediation models (e.g., Phyto-DSS, BALANS, Dynamic factor method, and Hung and Mackay model) are being evaluated for different contaminants, sorbents, and plants, and for integration into proposed compartment model. Additional LID Plant Monitoring will incorporate ground-based monitoring of green infrastructure (GI) facilities for estimation of fraction of intercepted photosynthetically active radiation (fiPAR), though that posed multiple operational challenges. Uninhabited aircraft systems (UAS) were found to enable efficient acquisition of multi-temporal normalized difference vegetation index (NDVI) data for GI site monitoring, through the workflow developed in Prettyman et al. (2020).

Results and Discussion

Four sorbents were compared in single-point batch experiments for the removal of heavy metals and PFAS. A series of synthetic and real stormwater matrices was used to select sorbents and determine stormwater matrix component effects on sorbent performance. Due to the differences

in properties, a series of sorbents is needed: Biochar Basic for heavy metals and RemBind® for PFAS. To date, this is one of the few studies addressing heavy metals and PFAS as co-contaminants and the only study evaluating sorbents for remediation of both classes together. Discrepancies in sorbent performance between synthetic stormwater and real stormwater indicate that synthetic stormwater is not a suitable alternative for lab-experiments. Decisions should be based on real, field-collected stormwater. Suspended sediment was the primary component in stormwater that resulted in decreased sorbent performance. However, suspended sediment had had less of an impact on Biochar Basic's removal of heavy metals because of complexations between heavy metals and organic matter. RemBind was more impacted than Biochar Basic by suspended sediment and so it is recommended to be placed behind Biochar Basic in a treatment train. Pretreatment of stormwater with Biochar Basic led to significantly increased removal of eleven out of twenty-one PFAS by RemBind.

A ten-week long greenhouse experiment was conducted to evaluate the phytoremediation potential of ten plants split into five groups: grasses, rushes, sedges, stemless dicots, and stemmed dicots. This is the fourth study, and the second greenhouse study, to explore phytoremediation as an option for PFAS. The mass balance was closed on eight out of ten plants and the soil-only controls, which had not been previously done. Because the mass balance was closed, mass accumulation factors (MAFs) were calculated, in addition to bioconcentration factors (BCFs) and translocation factors (TFs). Both BCFs and MAFs should be considered when selecting plants for phytoremediation scenarios. Out of the five plant groups, grasses and stemless dicots had the highest combined BCF and MAF, demonstrating the greatest potential for PFAS phytoremediation.

This work is some of the first to consider how biofilm formation and desorption affects the removal of heavy metals, nutrients, and DOC from real stormwater. Results from this work demonstrate that the environmental biofilms can form on sand, GAC and biochar with the greatest biofilm density forming on GAC and the lowest biofilm density forming on sand. The formation of these environmental biofilms increased the sorptive capacity of sand, GAC and biochar to remove copper and zinc from stormwater.

Using a tracer study, sediment-borne contaminant load on a per-size-fraction basis was quantified. The results showed contaminant load increased with decreasing particle size, as would be expected due to the larger surface area associated with smaller particles, with one exception of Fe which had greatest contaminant load for sizes 25-75 μm .

A new model for fine sediment transport in LID-like conditions was developed. The model also allows for representation of the "clogging" effect that occurs when high concentrations of fine sediment are present in the influent stormwater.

Overall, the treatment train system reduced turbidity from an average of 94 NTU at the influent to an average of 14 NTU at the effluent in the six monitored storms. A tendency of a slight increase in turbidity was, however, observed after Rembind treatment train for all six storms, which could be attributed to leaching fines. Across 6 storms, residence time of LID was about 90 minutes when the number of antecedent dry days were ≥ 1 . Biochar and Rembind Cells' residence time varied

from 10 - 37 minutes. The overall treatment system yielded significant reductions in TSS event mean concentrations, ranging from 84% to 97% across the six monitored storms.

The treatment train reduced total copper and total zinc by 17% - 84% and 54% - 90%, respectively. For three monitored storms, the treatment train was also consistent in removing dissolved copper by modest amount (5% - 30%) and dissolved zinc by 47% - 75%.

Preliminary work on the development and calibration of baseline SWMM model has been completed. However, inclusion of storm data collected in 2021-2022 in the model has not been completed.

Implications for Future Research and Benefits

Together, the results of this research indicate that Green Infrastructure can be developed and used to remove a wide array of potential pollutants at military sites, in order to minimize the recontamination of remediated sediment.

Objectives

The overall goals of this project were to: (1) develop innovative stormwater control and treatment technologies that improve stormwater management, prevent sediment recontamination, and add to the existing water supply, and to (2) develop watershed modeling of new stormwater control processes that focus on sediment-related contaminants to provide information on the efficiency needed and the number of systems deployed to prevent sediment recontamination and increase stormwater harvesting.

To achieve these overall goals, the four specific tasks of this SERDP were as follows:

Objective 1: Improve lab-scale mechanistic understanding of the fate and transport of PAHs, PCBs, PFASs, Cu^{2+} , and Zn^{2+} through commercially available stormwater sorbents (bioswale soil, GAC, Biochar Basic™, EarthLite™, and RemBind®). This Task was further extended past the original proposal and budget to accommodate SERDP requests for including stormwater from DOD site Willow Grove and additional sorbent analysis (Calgon). This significantly changed the original timing and progress for further aspects of the project as these were not originally part of the scope of this work.

Objective 2: Improve lab-scale, mechanistic understanding the fate and transport of heavy metals, PAHs, PCBs, and PFASs through vegetated bioswales containing native grasses, broad-leaf plants, and their associated microbial communities. This further included microbiome sequencing and analysis to determine performance markers for stormwater and plant/microbiome dependencies.

Objective 3: Conduct field scale testing to investigate the fate and transport of PAHs, PCBs, PFAS, heavy metals, nutrients, total solids, and organic carbon in three types of Green Infrastructure BMPs, for multiple storm events. The primary goal of this objective will be to characterize the fate and transport of PFAS-associated particulates in the field and use the results of the lab-scale studies (from Objectives 1 and 2) to design, deploy and evaluate a novel treatment train at the field-scale, under a variety of storm intensities and environmental conditions.

Objective 4: Develop a new module for improving the simulation of plant-water-soil interactions for standard water quality parameters, and sediment-associated PAHs, PCBs, and PFAS in the USEPA SWMM model, and validate the improved model for multiple storm events using the field experiment data collected in Task 3.

This Final Report for SERDP ER18-1230 describes the research conducted to complete all Tasks and details of specific subtasks. Further progress about continuing and future progress towards aspects of Task 3 (field-scale studies) and 4 (modeling) are further noted.

Background

Task 1

Task 1 will utilize lab-scale batch isotherm and column experiments to characterize the removal of PAHs, PCBs, PFASs, Cu^{2+} , and Zn^{2+} by commercially available sorbents. Additionally, the column studies will characterize the potential desorption of contaminants during periods of interrupted hydraulic loading. The sorbents to be tested include bioswale soil (25% mint compost, 25% municipal compost, and 50% native clay soil), granulated activated carbon, Biochar Basic™ (sourced from Douglas fir), EarthLite™ stormwater filter media (composite of hazelnut shell biochar, expanded shale, compost, and oyster shells), and RemBind® media (mixture of activated carbon, aluminum hydroxide, and kaolin clay). This Task was further extended past the original proposal and budget to accommodate SERDP requests for including stormwater from DOD site Willow Grove and additional sorbent analysis (Calgon).

Task 2

Task 2 utilized lab-scale planted mesocosms to characterize the fate, transport and remediation of heavy metals, PAHs, PCBs, and PFASs through a typical vegetated bioswale. The planted mesocosms contained one of ten different plants (five grasses and five broad-leafed plants) that are currently used in vegetated stormwater bioswales in the Pacific Northwest (Jurries, 2003). The careful characterization of plant physiology, plant morphology, and rhizosphere-associated microbiomes was correlated with mesocosm performance to help translate the results to native plants in other regions of the United States. Additionally, the lab-scale planted mesocosms was exposed to a variety of wetting regimes to mimic different weather patterns across the United States. Finally, to determine the role that subsurface redox conditions play, the mesocosms was kept either aerobic or anaerobic through the use of an effluent riser to maintain a constant saturation zone within the system.

The inclusion of plants within a given green infrastructure / low impact development (LID) design was intended, in part, to help meet treatment goals which may vary greatly from site to site. Much currently installed stormwater infrastructure seeks to treat sediments, metals, nutrients, and, in some cases, PFASs. The treatment performances of particular plants are not presently predictable, but are nonetheless critical to successful treatment. Therefore, systematic investigation of a variety of plants in a controlled, green house setting informed not only the improved treatment train design (Task 3), but further reveal how plant physiology and phylogeny may be related to the treatment of the manifold contaminants in municipal and DoD-site associated stormwater.

Task 3

Low Impact Development (LID) has gained considerable popularity among DoD sites, as well as municipal sites worldwide, as an overarching approach to development that helps restore hydrologic processes and reduce the impacts of stormwater on the environment. LID consists of a suite of site design approaches and stormwater BMPs that use ecological systems and processes to store, slow, infiltrate, and treat stormwater runoff. Many of these BMPs include systems such as bioretention cells, rain gardens, bioswales, vegetated rooftops (or, green roofs), and rain

barrels. These BMPs provide not only hydrologic benefits, but are also promoted for complementary co-benefits, such as water quality improvement, reduction in urban heat island effects, ecological habitats, and community well-being. It is important to note that, while the adoption of these systems is gaining popularity in communities across the world, many of these assumed co-benefits are still under-studied and not well understood. For example, in context of this project, it is unknown how well these systems would help store and treat contaminants, such as PAHs, PFASs, and metals. Methodologies need to be developed for monitoring such treatment systems, quantify their performance, and calibrate and/or validate numerical models. Further, limited research exists on how best to design treatment train strategy to stormwater management that optimize hydraulic and contaminant removal efficiencies for contaminants ranging from particulates to dissolved substances, including nutrients, heavy metals, PAHs, and PFAS.

Task 4

The USEPA's Storm Water Management Model (SWMM) is a popular and extensively tested watershed-scale model for simulating, designing and optimizing stormwater drainage systems in urban areas, including GI (Rossman, 2010). While the model has extensive hydrology-hydraulic methods for dynamic simulation of stormwater runoff volumes during single event storms and long-term (continuous) rainfall in urban areas, it uses simplistic buildup/wash-off function coefficients, first order decay coefficients, and removal equations for the fate and transport of contaminants (Wong et al., 2006; Huber et al., 1988; McAlister et al., 2003). Additionally, there is a critical lack of literature to validate these equations for modeling PAHs, PFASs, and heavy metals, beyond the standard water quality parameters (Elliott et al., 2007; Zellner et al., 2010). As urban communities across the U.S. begin to deploy these practices close to where people live and work, the impact on water quality and the potential exposure from multiple water quality parameters, such as chemicals, pathogens, and emerging contaminants is increasingly important and needs to be quantified.

Materials and Methods

Task 1

The primary goal of Task 1.1 was to screen the ability of five different sorbents (bioswale soil, GAC, Biochar Basic™, EarthLite™, and RemBind®) for their ability to remove heavy metals (Cu^{2+} and Zn^{2+}) and five model PFASs (PFBA, PFOA, PFHxS, PFOS, and FtSaB) in a synthetic stormwater that resembles roadway runoff (including 0.185 mM NaHCO_3 , 1.0 mM NaCl , pH 6.0) (Nason et al., 2012). The justification for the use of synthetic stormwater was to give a “best case scenario” baseline that is not affected by other stormwater constituents, whose concentrations can be highly variable and site specific (Pitt et al., 2018).

The model PFASs were chosen to give a range of physical and chemical properties including short-chained PFASs (e.g., PFBA), long-chained PFASs (e.g., FtSaB), carboxylic PFASs (e.g., PFBA, PFOA), sulfonic PFAS (e.g., PFHxS and PFOS), zwitterionic PFASs (e.g., 6:2 FtSaB) and those with drinking water limits (e.g., PFOA and PFOS) (Figure 1). Cu^{2+} and Zn^{2+} were chosen as the representative heavy metals because they are commonly found in stormwater, have an environmental toxicity, and are regulated in stormwater permits (Kayhanian et al., 2008; Gobel et al., 2007). Due to their high K_{ow} 's, PAHs and PCBs were expected to be removed much more easily than Cu^{2+} , Zn^{2+} , and PFASs (Krauss and Wilcke, 2001; Zhang et al., 2019). Thus, to expedite the initial screening process, PAHs and PCBs were excluded with the assumption that if the sorbents could remove heavy metals and/or PFASs then PAHs and PCBs would also be removed.

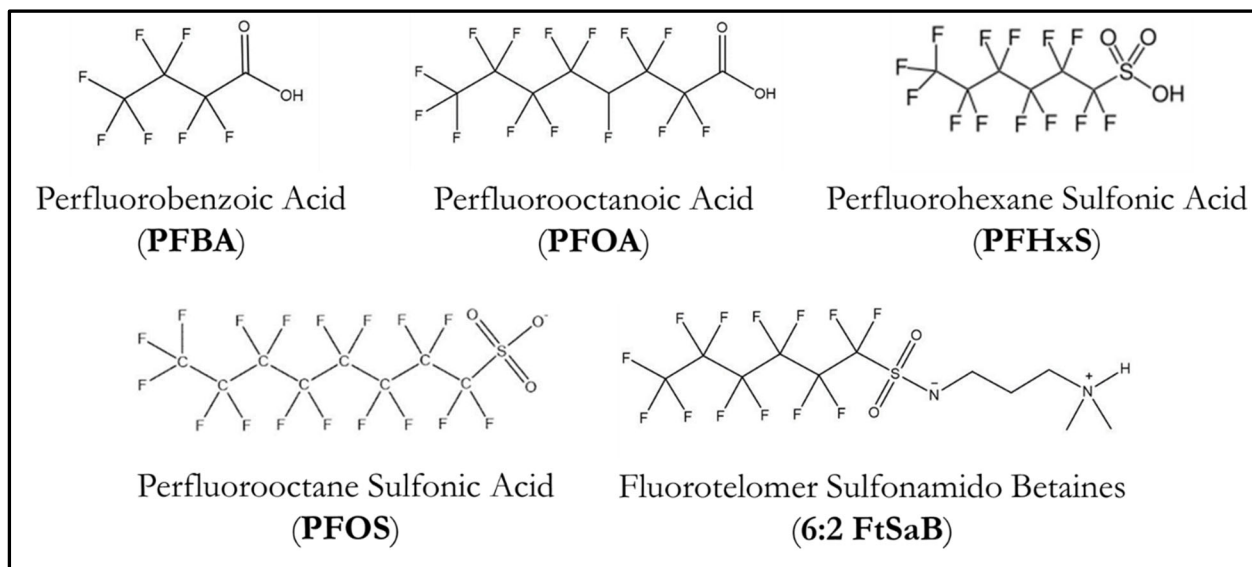


Figure 1. Selected model PFASs containing a range of properties such as chain length, polar head groups and charge.

The five sorbents were chosen to be screened for a variety of reasons. Bioswale soil (25% mint compost, 25% municipal compost and 50% native clay soil) was chosen to serve as a baseline of expected contaminant removal in a bioswale in the absence of additional sorbents. Granulated

activated carbon (GAC) was chosen as an industry standard for the removal of water contaminants. It should be noted that the GAC used in these experiments was lab-grade and not the same kind used in the field. Thus, experiments in Task 1 will be repeated using Calgon F400, a commercial GAC currently used at DoD sites dealing with PFAS contamination.

Biochar Basic™ is a commercially available Douglas fir-based biochar that has been successfully used for metal remediation from stormwater at Navy sites in the Puget Sound and Pearl Harbor. EarthLite™ is a commercially available biochar composite made from hazelnut shells, expanded shale, compost, and oyster shells (EarthLite™ Biochar Medias). EarthLite™ has been successfully used in the Pacific Northwest for the remediation of heavy metals from stormwater. RemBind® is a mixture of activated carbon, aluminum hydroxide, and kaolin clay that has been used to treat PFASs in contaminated soils, groundwater, and surface waters (Lath et al., 2018; Sorengard et al., 2019).

All sorbents were washed, dried, and sieved through 30 mesh (0.595 mm) screens before testing. For PFAS testing, 5 mg of sorbent was placed into triplicate batch bottles containing synthetic stormwater spiked with PFASs (500 ng/L concentration per PFAS). For heavy metal testing, 15 mg of sorbent was placed into triplicate batch bottles containing 25 mL of synthetic stormwater containing Zn^{2+} and Cu^{2+} at one of three ratios (200:50, 400:100, or 1000:250 ppb $\text{Zn}^{2+}:\text{Cu}^{2+}$). All batch bottles were tumbled for 24 h at 20 °C before final analysis of PFAS and heavy metal concentrations by LC MS-MS or ICP-MS, respectively.

The primary goal of Task 1.2 was to repeat the tests of Task 1.1 but replace the synthetic stormwater with real stormwater collected from our bioswale research facility to determine how the presence of additional stormwater constituents (e.g., dissolved organic carbon, Fe^{3+} , etc.) influenced each sorbent's ability to remove heavy metals and PFASs. All collected stormwater was filtered through a 0.44 μm filter to remove suspended solids. As with Task 1.1, the filtered collected stormwater was spiked with either PFASs (500 ng/L concentration per PFAS) or with Cu^{2+} and Zn^{2+} to achieve final concentration ratios of 200:50, 400:100, or 1000:250 ppb $\text{Zn}^{2+}:\text{Cu}^{2+}$.

The primary goal of Task 1.3 was to identify which stormwater constituents in our collected stormwater is responsible for any removal efficiencies observed between Tasks 1.1 and 1.2. To complete this task, the chemical composition of the collected stormwater from Task 1.2 was thoroughly characterized. Then, the experiments in Task 1.1 were repeated by altering the synthetic stormwater in a piecemeal fashion to mimic the collected stormwater chemical composition. In this way, we were able to isolate which stormwater constituent(s) are primarily responsible for sorbent performance differences between Tasks 1.1 and 1.2.

The primary goal of Task 1.4 was to create lab-scale stormwater treatment trains that can be used to demonstrate the removal efficiency of the treatment train design and provide data to predict breakthrough in the pilot-scale system (Task 3.3). This was accomplished using a set of rapid small-scale columns (RSSCs) in series. The final treatment train design was then installed based on these results, have stormwater flowing through planted soil and then sand before moving on to the sorbents, the lab-scale treatment train will use effluent stormwater from our bioswale research facility (to simulate the treatment by plants) that has been filtered through a 0.44 μm

filter (to simulate the treatment by sand). The lab-scale treatment train will consist of two RSSCs with the first containing the best sorbent for heavy metal, PAH, and PCB removal and the second containing the best sorbent for PFAS removal. Additional pre-treatment RSSCs may be added, as needed, based on the results from Task 1.3. The system will be run until breakthrough is observed. To aid in up-scaling the results, this system will be run twice using sorbents of two different diameters (0.11 mm and 0.61 mm).

The primary goal of Task 1.5 was to determine how intermittent flow affects the removal efficiency of the stormwater treatment train. Unlike groundwater or surface water remediation schemes, stormwater has an intermittent flow pattern with periods of flow followed by weeks to months with no flow. This quiescent time may allow for the desorption of contaminants from the sorbents into the pore-water before leaving the system during the next storm event. To understand this phenomenon more fully in our treatment train system, once breakthrough is observed, the treatment train will be flushed with synthetic stormwater that mimics the collected stormwater, except that heavy metals, PAHs, PCBs, and PFASs will be absent. This was intended to quantify what mass of the contaminants were only loosely bound to the sorbents. After that, the flow to the system will be shut off for periods of days and weeks to determine how the quiescent period affects the slow release of more tightly bound contaminants.

This final task was not fully carried out due to many factors, including delays due to COVID-19, the additional costs of materials and labor due to that delay, and the time intensive tasks of Objective 1 tasks remaining. However, some preliminary tests were performed by running desorption experiments on the same columns tested in Task 1.4 to see what fraction of the nutrients and heavy metals could be mobilized off the sorbents in the presence or absence of the biofilms. Initial results demonstrated that the presence of biofilms significantly reduce the desorption of copper. This suggests that the presence of biofilms on the sorbents both increases heavy metal removal and limits their desorption from the sorbents.

Task 2

Ten native Pacific Northwest plants were selected and included a combination of classes and families (

Table 1). Six of each plant were purchased locally and planted in high density polyethylene (HDPE) buckets (3.78 L) from Berlin Packaging (Chicago, IL). The buckets contained a drainage layer of 300 mL of course gravel and 4.3 kg of soil. Soil consisted of a 50/50 mix by volume of sand and soil, collected from the Oregon State University Benton country Green Stormwater Infrastructure Research (OGSIR) facility from a cell that had no previous exposure to stormwater. Soil from OGSIR was sieved through a 4mm sieve and homogenized with sand. During transplanting, initial soil samples were collected and analyzed for PFAS, organic carbon, and pH.

Table 1: Plants examined for sorbency and retention of contaminants.

<u>Grasses</u>		<u>Broad-leaved Plants</u>	
Scientific Name	Common Name	Scientific Name	Common Name
<i>Danthonia californica</i>	California Oatgrass	<i>Lupinus polyphullus</i>	Large-leaved Lupine
<i>Deschampsia cespitosa</i>	Tuft Hair Grass	<i>Sidalcea campestris</i>	Meadow Checker Mallow
<i>Carex obnupta</i>	Slough Sedge	<i>Mahonia repens</i>	Creeping Oregon Grape
<i>Carex densa</i>	Dense Sedge	<i>Achillea millefolium</i>	Common Yarrow
<i>Schoenoplectus acutus</i>	Hardstem Bulrush	<i>Gaultheria shallon</i>	Salal

Simple randomization was employed weekly to shuffle the placement of each unit to ensure spatiotemporal homogeneity of greenhouse conditions (e.g. sunlight, temperature, humidity). For ten weeks, stormwater collected from OGSIR was spiked with PFAS and applied to all plants and soil-only controls.

For ten weeks, experimental units were watered once per week. On the start of every watering day, plants and soil-only controls were weighed to get an initial mass. Then each plant and soil control was watered to ensure they reach saturation, while also providing enough effluent for chemical (PFAS, dissolved organic carbon, pH) analysis using the following equation:

$$Water\ added\ (g) = avg\ saturation\ mass - mass_{total\ system} + 300\ g - mass_{water\ out}$$

(Equation 1)

Where the average saturation mass is a moving average updated on a weekly basis, mass of the total system includes the plant (aside from soil-only controls), soil, gravel, and bucket, and the mass of water out (effluent) is based on how much water was in the effluent the previous week. A constant of 300 g was based on repeated initial measurements leading up to the greenhouse experiment. The stormwater was spiked with 13 PFAS at 1,000 ng/L and homogenized by mixing prior to watering the plants and soil-only controls. Nutrients, solids, as well as zinc and copper were present in this stormwater.

After watering, the plants and soil-only controls sat for five hours with the valve closed, then the valve was opened for 20 min to collect effluent and then the plants and soil controls were weighed again. The effluent was weighed after collection. Four influent samples were collected during each watering and used to calculate the average concentration of influent constituents. Field blanks were also collected each week and consisted of HPLC grade water in an open container during spiking, watering, and sample collection. Field blanks were consistently below the limit of detection or limit of quantification (<LOD and <LOQ, respectively) for all 13 PFAS and both metals.

For nine out of ten weeks, effluent samples were composited from the replicates of each plant type and analyzed. However, week 4 was randomly selected to analyze all plants individually to determine parameter variability across all units. The percent relative standard deviation (% RSD)

in plant effluent samples taken on week four was consistently less than 30% for the 13 PFAS and less than 10% for copper and zinc.

Weeds were observed in all plants and soil-only controls. While the objective of this study was not to evaluate the removal of PFAS by weeds, it was recognized that weeds are an environmentally relevant parameter and so they were allowed to remain. However, at the end of 10 weeks, the weeds were harvested, homogenized, and analyzed.

At the end of ten weeks, all plants and soil-only controls were watered with PFAS-free stormwater to displace the aqueous phase remaining in the soil pore volume. The displaced water was collected and analyzed for PFAS. Plants were then separated into leaves, stems, weeds, roots, and soil and soil-only controls were separated into weeds, roots, and soil. Each component was homogenized with a blender, and then randomly composited into three samples. For example, out of the six yarrow plants, there were three leaf composites, three stem composites, three weed composites, three root composites, and three soil composites. Plants were composited to ensure there was enough PFAS mass present to be above the limit of detection (LOD), but with enough replication ($n=3$) to allow for statistical analysis.

Extraction and Instrumental Analysis

Aqueous, soil, and plant samples were each extracted with corresponding methods. For each set of extractions, one sample was analyzed with $n=4$ replicates to calculate a % RSD. Process blanks were including with every sample set to account for background PFAS. For aqueous, soil, and plant matrices, the process blank was DI water, PFAS-free sand, and a PFAS-free composite of plant tissue. All PFAS extracts were analyzed by large volume (900 μL) injection onto a C18 column using HPLC. Aqueous PFAS samples were initially analyzed via HPLC-tandem mass spectrometry (HPLC-TQD-MS) for the target PFAS, but samples from weeks one, nine, and ten were analyzed by HPLC-quadrupole time of flight (HPLC-QToF)-MS. All soil and plant extracts were analyzed for PFAS via HPLC-QToF-MS. All metals samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). All aqueous 'total' metals samples as well as all plant and soil metals samples were preprocessed by microwave digestion using standard methods. All dissolved metals samples were filtered through 0.45 micron filters.

Task 3

In Task 3.1, new sensors were installed at the OGSIR field site to obtain time-resolved observations of the treatment train during storm events. Optical backscatter sensors (OBS) were used to measure turbidity of stormwater at each stage of the treatment train. Four OBSs were mounted in the 4" riser pipes at the LID inlet, LID outlet, between the two sorbent storage bins, and at the treatment train outlet. Each OBS sensor was calibrated against a turbidity standard (formazin), and sensor enclosures were constructed that ensured the calibrations would not be affected when the sensors were deployed in the 4" risers. A custom data acquisition system was developed to transmit OBS data wirelessly from the sensors to a central data logger. Turbidity data from each sensor is logged at 1 Hz continually, and data are automatically backed up to an off-site server daily. In addition to turbidity sensors, Barodiver pressure transducers were also installed in the riser pipes to measure water levels at the locations of the OBS sensors.

In Task 3.2, experiments were conducted to characterize the spatial pathways of sediments, sediment-borne contaminants and dissolved contaminants over multiple storm events at seasonal time-scales. Specifically, this task developed a methodology using dual-signature (fluorescent/magnetic) silt-sized tracer particles obtained from Partrac Ltd. (Collins et al., 2013; Black et al., 2007), that allowed us to quantify the spatial and temporal distribution of fine sediment flowing over a natural soil bed having the same sediment and hydraulic characteristics as the LID module in the developed treatment train. The experimental design for the tracer study was based in part on a particle size distribution (PSD) analysis of the OGSIR soil, which used X-ray microanalysis and hydrometer analysis for particle diameters $<70\ \mu\text{m}$, and dry sieving for particle diameters $>70\ \mu\text{m}$. A size-specific analysis of particle-borne metals was also performed: Batch equilibrium tests were done using ICP-MS, for 50 mL samples and three sediment size fractions $<20\ \mu\text{m}$, $20\text{--}75\ \mu\text{m}$, and $75\text{--}90\ \mu\text{m}$; samples were shaken for 24h until equilibrium was reached, with an initial contaminant concentration 500 ppb Fe, Zn, and Cu.

A flume was constructed in which to perform the tracer study, shown in Figure 2. The flume injects tracer-laden water at a constant flow rate and tracer-concentration, which then flows over an inclined bed of fully-saturated natural soil sourced from the OGSIR field site. The introduced tracer is monitored to determine the space-time-dependent deposition of tracer onto the soil surface, which determines overall transport. Specifically, tracer was measured using a custom camera hood apparatus, Figure 3. The camera hood enclosure contains an ultraviolet light source that excites fluorescence in the tracer particles, which is then recorded by a camera (FLIR BlackFly). A narrow-bandpass filter on the camera isolates the tracer's fluorescence emission wavelength and thereby excludes light reflected from non-tracer particles. Calibration experiments showed the light intensity measured by the camera is linearly related ($R^2 = 0.9996$) to the bulk concentration of tracer present in the soil. Hence the camera hood apparatus can be used to create a map of the tracer concentration on the flume surface. Importantly, the tracer-camera methodology does not disturb the soil bed, which was critical for our experiment design.

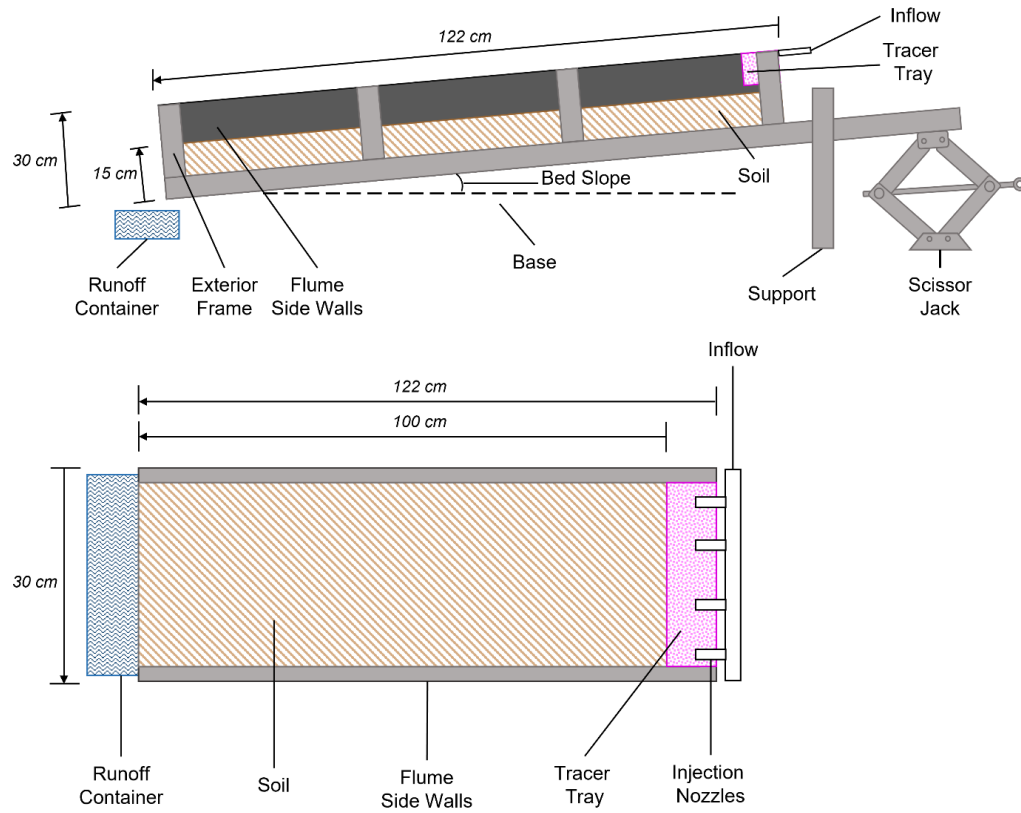


Figure 2: Flume used for experimental soil tracer study.

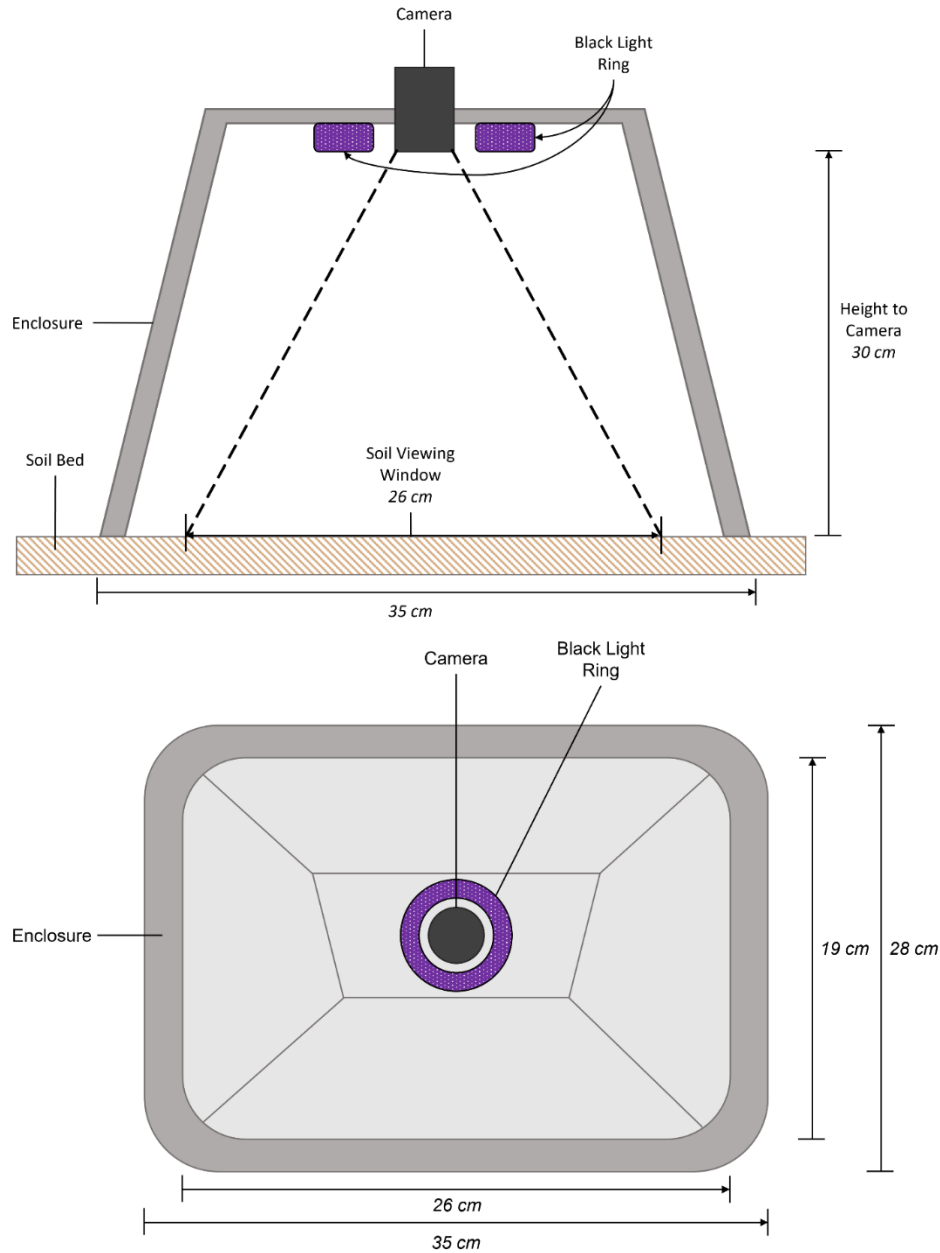


Figure 3: Camera hood used for measuring sediment tracer concentration in experimental soil tracer study.

In Task 3.3, insights obtained in Objectives 1-2 on commercial sorbents and plants best suited for treating heavy metals and PFAS in stormwater were used to design and implement a prototype treatment train installation in the field at the OGSIR facility in Corvallis, OR. The treatment train was designed to have three stages: bioretention cell with downward flow, followed by upflow through macrobins containing sorbent Biochar, and finally followed by upflow through macrobins containing sorbent Rembind (specifically, in the form of Aquagate aggregates). To maximize the number of contaminants removed by plants (Objective 2) and maximize dry-weather resilience, two types of grasses (specifically, the *Juncus Patens* rush and *Carex Obnupta* sedge) were selected for the bioretention cell. The sizing of the treatment train

was based on a maximum design flow of 2.5 gpm and for expected residence time of up to 30 minutes in the sorbent bins. Because of large uncertainties in field-scale values of hydraulic conductivity and porosities of sorbents, sorbent porosities were assumed to range from 0.46 to 0.8 (based on literature) and hydraulic conductivities were assumed to be close to lab measurements (bioretention soil K of $6.30\text{E-}05$ m/s, Biochar Basic K = $8.08\text{E-}03$ m/s, and Rembind Aquagate K = $1.00\text{E-}03$ m/s) were used in the design process. Because of COVID-19 related shut downs, the construction of the treatment train was delayed to December 2020. These delays created additional delays in field data collections and advanced modeling efforts in Task 4. Figure 4–Figure 6 include images on the conceptual design of treatment train. Figure 7–Figure 8a display images of the treatment train during and after construction. Figure 8b illustrates the set up used to install OBS turbidity sensors and Barodivers (water level monitoring) in vertical risers of the treatment train (Junctions 0-4 in Figure 4). Figure 9a illustrates how commercial sorbents were packed in compost socks and placed on top of grates in food-safe macrobins (i.e., Biochar cells and Rembind cells in Figure 4–Figure 6). Figure 9b–Figure 10 illustrate the challenges that were experienced with fines released from the new bioretention system, Biochar material, and Rembind material when flows went through the new system. To minimize contamination by fines, Biochar was placed after first few flushes of stormwater through the bioretention cell had reasonably declined the fines exported by the bioretention cell. Similarly, Aquagate material was finally placed in the Rembind cells, after Biochar cells had reasonable amount of decline in fines exported by new Biochar material. A similar leaching behavior was observed when stormwater flushed through Rembind (specifically, Aquagate) cells. Overall, while the system construction and set up was completed by April 2021, the treatment train was not considered ready for testing until September 2021 after the first few rains had flushed fines.

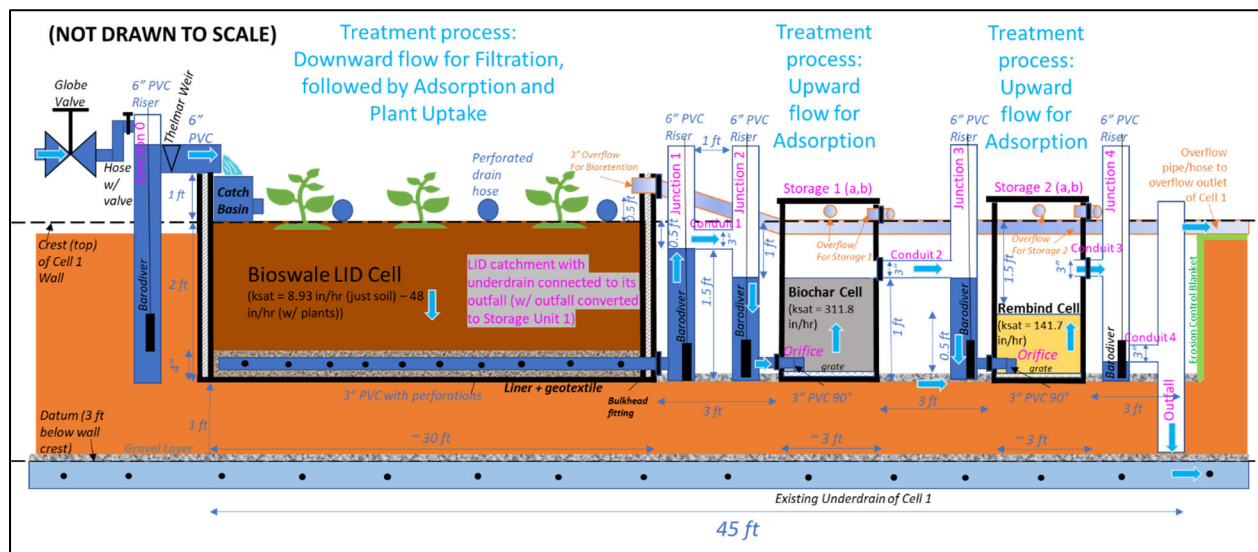


Figure 4: Treatment train design consisting of series of bioswale cell and sorbent cells

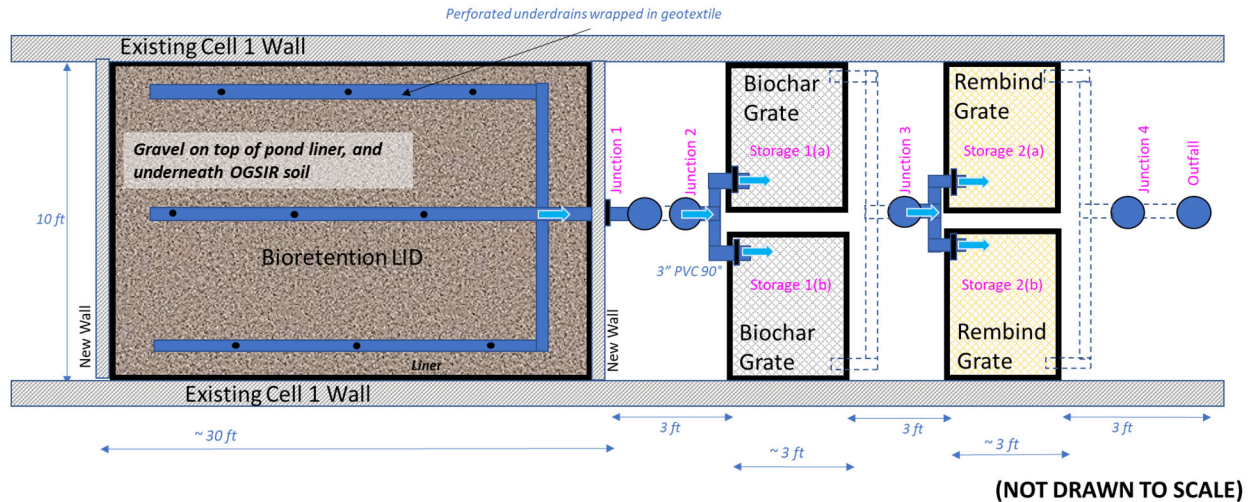


Figure 5: Bird's eye view of lower section of treatment train design

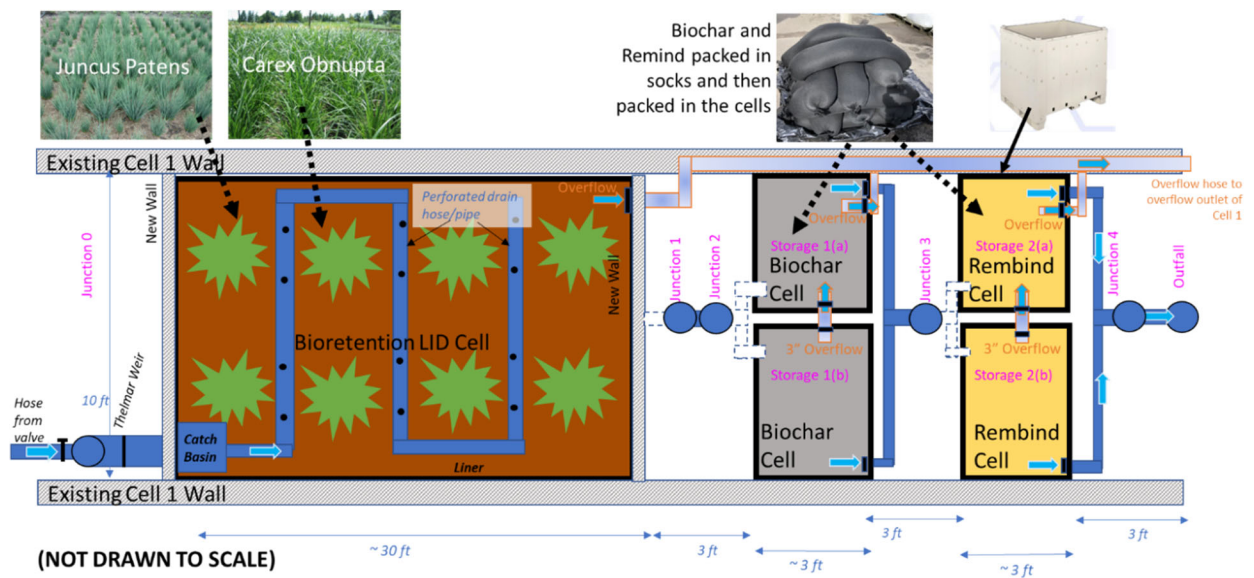


Figure 6: Bird's eye view of top of treatment train design

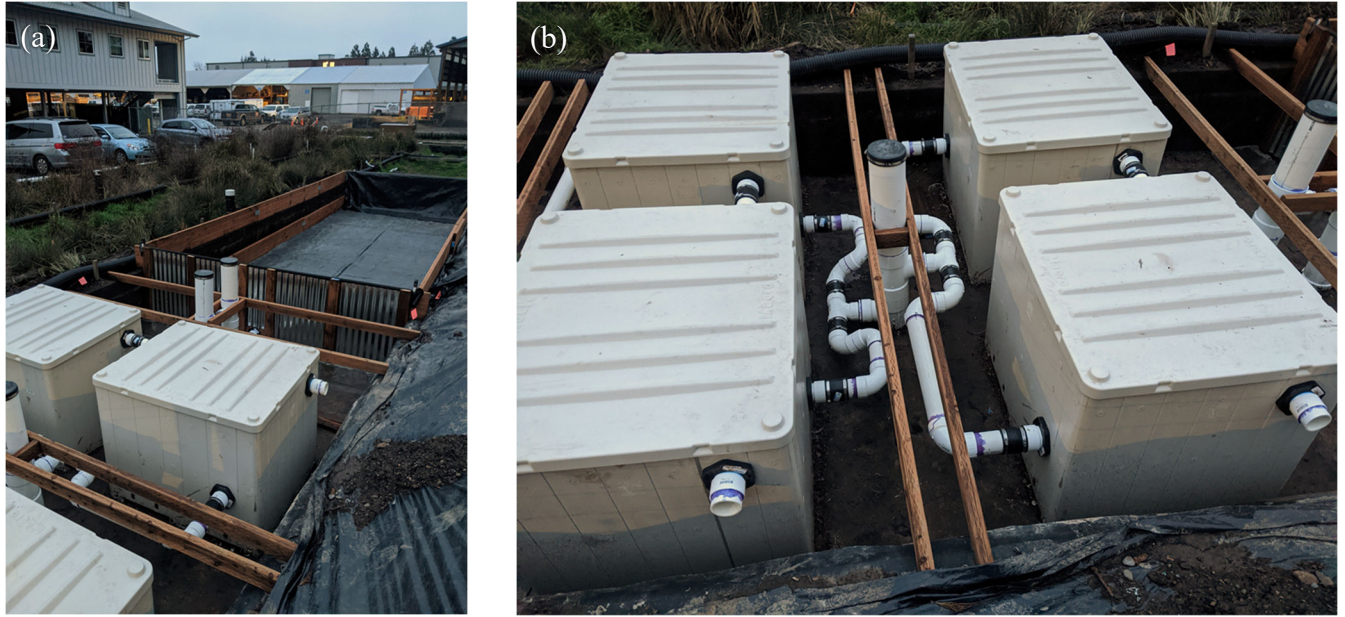


Figure 7: (a) Construction of Treatment Train; (b) Pipe connections between cells, including vertical PVC risers for stormwater sampling.



Figure 8: (a) Completed treatment train; (b) Installation of Flow and Turbidity in-situ sensors in risers for real-time monitoring to support Task 3.2, 4.1 and 4.2.



Figure 9: (a) Placement of Biochar and Aquagate (Rembind) in compost socks within macrobins; (b) Leaching of fines from LID before biochar is placed in macrobins.

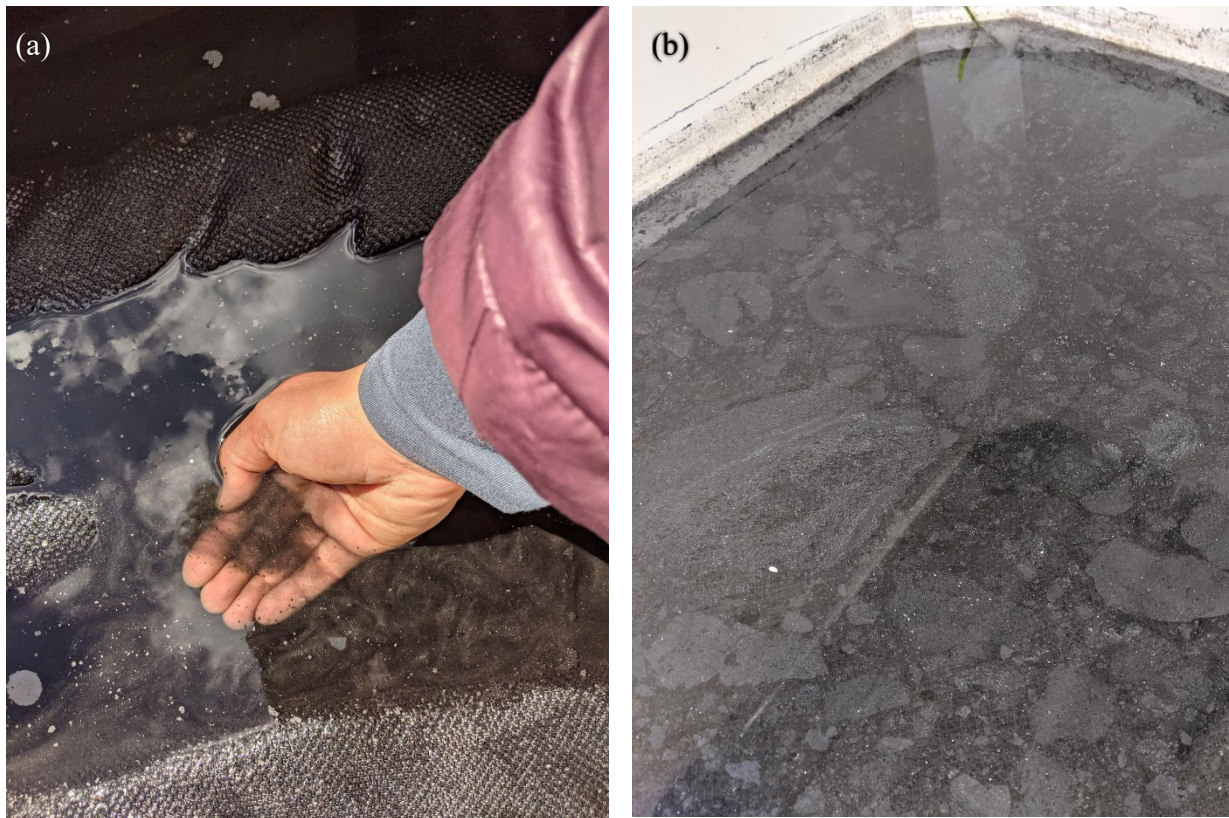


Figure 10: (a) Leaching of fines from biochar after new biochar is placed in macrobins; (b) Leached biochar fines floating on the stormwater in the macrobin.

Task 4

Calibration and Validation of existing SWMM model

In Task 4.1, a baseline SWMM model was developed to simulate the hydrologic flow and water quality processes in the treatment train. While preliminary water level data measured by Barodivers were initially used to test model setup, comprehensive storm sampling was conducted in Fall 2021-Spring 2022 as part of Task 3.3 using OBS turbidity sensors, Barodivers, ISCO samplers, and field probes for flows entering the bioretention cell, after bioretention cell, after Biochar cells, and after Rembind cells. The new data collected will inform any additional remaining tasks related to calibration and validation of existing SWMM model. The calibration process is currently partially completed and will be finalized in late 2022.

Development of new compartment-based model components in SWMM

Task 4.2 constituted a plan for compartment-based modeling approach, which would be later integrated into the SWMM model as a new plant sub-model, was developed for the fate and transport of heavy metals in LID bioretention cell. The plan included: (a) development of rapid monitoring approach for estimating plant growth and productivity using Uncrewed Aircraft Systems (UAVs) so that the plant productivity in the new SWMM could be calibrated, and (b)

development of a sub-model that can use partition coefficients for estimating the extraction and accumulation of heavy metals in three different sections of the plants (i.e., roots, stems, and leaves). For the Biochar and Rembind cells, first-order rate equations was planned to be used for modeling the concentration of heavy metals in the outflow of the sorbent cells. Note that while the task related to UAV-based monitoring approach was completed and are reported in Task 3.3 results below, details on the validation of the compartment-based model using this plant data as well as new water quality data from storms sampled in 2021-2022 are not currently available, since it was not completed because of COVID-19 delays and hurdles.

Results and Discussion

Task 1

For Task 1.1, we found that Biochar Basic™ has superior removal of Cu^{2+} ($93 \pm 1\%$) and Zn^{2+} ($74 \pm 4\%$) compared to the other sorbents which removed roughly 35-49% of the Cu^{2+} and 21-44% of the Zn^{2+} (Table 2). The superior removal of Biochar Basic™ is most likely due to its cation exchange capacity (CEC) of 709 ± 138 meq/kg, which is significantly greater than the other sorbents (Table 3).

For PFAS removal, RemBind® was the most effective at removing PFASs across the board ($> 84 \pm 10\%$), followed by GAC ($> 77 \pm 4\%$). EarthLite™ was most effective at removing PFHxS, PFOS, and FtSaB ($28 \pm 18\%$, $55 \pm 21\%$, and $83 \pm 10\%$, respectively) while bioswale soil and Biochar Basic™ was ineffective at removing PFASs. It should also be noted that none of the sorbents were effective at removing the shortest PFAS, PFBA.

Table 2: Percent removals of model PFASs, Cu^{2+} , and Zn^{2+} in clean synthetic stormwater by selected sorbents.

Synthetic Stormwater														
Sorbent	PFBA		PFOA		PFHxS		PFOS		FtSaB		Cu ²⁺		Zn ²⁺	
	%	95%	%	95%	%	95%	%	95%	%	95%	%	95%	%	95%
	Removal	CI	Removal	CI	Removal	CI	Removal	CI	Removal	CI	Removal	CI	Removal	CI
Soil	-1	8	-2	8	-1	12	7	9	14	16	47	0	41	1
GAC	-18	16	77	4	79	3	79	8	78	13	35	2	21	4
Biochar	14	54	-9	27	-11	28	2	20	14	62	93	1	74	4
EarthLite	11	23	28	19	28	18	55	21	83	10	49	0	44	6
RemBind	-5	33	96	7	92	8	84	10	100	2	41	1	30	4

Table 3: Cation exchange capacity (CEC) of the tested sorbents.

Sorbent	CEC (meq/kg)	95% CI
Soil	156	44
GAC	223	44
Biochar	709	138
EarthLite	187	7
RemBind	20	13

For Task 1.2, we found that in the presence of collected stormwater all five sorbents had lower removal efficiencies for heavy metals and PFASs compared to when they were in the presence of synthetic stormwater (Table 4). Under collected stormwater conditions, all five sorbents behave similarly in regards to Cu^{2+} removal with removal efficiencies ranging from $24 \pm 0\%$ to $30 \pm 0\%$. Likewise, Zn^{2+} removal efficiencies began to cluster. EarthLite™ demonstrated the greatest Zn^{2+} removal at $23 \pm 1\%$ while bioswale soil, Biochar Basic™, and RemBind® had Zn^{2+} removal

efficiencies of 14 ± 0 to $16 \pm 1\%$. Surprisingly, the GAC sorbent had the poorest Zn^{2+} removal efficiency at $5 \pm 2\%$.

For PFASs, RemBind® showed significant removals of only PFOS and FtSaB ($15 \pm 10\%$ and $100 \pm 2\%$, respectively) while EarthLite™ only removed FtSaB ($90 \pm 12\%$). Bioswale soil and Biochar Basic™ were ineffective at removing PFASs under these conditions. GAC, however, was the most effective sorbent at removing PFASs under these conditions (PFOA: $9 \pm 2\%$; PFHxS: $13 \pm 3\%$; PFOS: $18 \pm 1\%$; FtSaB: $40 \pm 9\%$), although removal efficiencies were less than synthetic stormwater conditions.

Table 4: Percent removals of model PFASs, Cu^{2+} and Zn^{2+} in by selected sorbents in collected stormwater (from the OSU-Benton County Green Stormwater Infrastructure Research facility [OGSIR]) containing dissolved organic carbon, Fe, and other constituents.

OGSIR Stormwater														
Sorbent	PFBA		PFOA		PFHxS		PFOS		FtSaB		Cu ²⁺		Zn ²⁺	
	%	95%	%	95%	%	95%	%	95%	%	95%	%	95%	%	95%
	Removal	CI	Removal	CI	Removal	CI	Removal	CI	Removal	CI	Removal	CI	Removal	CI
Soil	-14	11	-17	13	-12	17	-7	16	-4	48	24	0	16	1
GAC	2	4	9	2	13	3	18	1	40	9	29	0	5	2
Biochar	0.5	18.5	-14	4	-2	7	-8	2	-67	39	25	0	15	1
EarthLite	-23	23	-17	17	-9	6	-3	2	90	12	29	0	23	1
RemBind	-1	11	-12	2	-6	8	15	10	100	2	30	0	14	0

A chemical composition analysis of the collected stormwater (Table 5) revealed that it was high in dissolved organic carbon (DOC; 12.4 ppm-C) and very high in Fe (3,048 ppb). These two constituents may help explain the decreased removal efficiencies under collected stormwater conditions.

For instance, Cu^{2+} is known to chelate with DOC, and thus DOC removal may then dominate Cu^{2+} removal (Breault et al., 1996). This could mask the sorbent's ability to remove Cu^{2+} , resulting in similar removal efficiencies across all sorbents, as seen in this study (Table 4). Additionally, the DOC may also coat the sorbents resulting in a surface layer that is dominated by hydrophobic interactions. This may help explain why only the longest chained PFASs (e.g., FtSaB) were significantly removed under collected stormwater conditions.

The very high levels of Fe may also play a role in the decreased performance of the sorbents. In the removal of Cu^{2+} and Zn^{2+} , the Fe may outcompete Cu^{2+} and/or Zn^{2+} for binding sites on the sorbents. Additionally, if a PFAS removal mechanism is due to cation exchange capacity, a very high Fe background may interfere with that process.

Experiments were conducted to tease apart which stormwater constituents are driving the reduced removal capabilities of the sorbents. Additional experiments were also performed with PFAS contaminated stormwater collected from the Naval Air Station Joint Reserve Base, Willow Grove (kindly provided by Mr. Jason Speicher). The chemical composition of this stormwater is

was analyzed and removal efficiency experiments were run in a manner similar to those in Task 1.2. Thus, these experiments provided additional data points that helped determine how stormwater composition affects the removal efficiency of these sorbents.

Table 5: Chemical constituent makeup of the collected OGSIR stormwater used in the sorbent screening studies.

OGSIR Stormwater Composition			
Constituent	Concentration	Constituent	Concentration
Alkalinity	27.8 ppm as CaCO ₃	Cl ⁻	1.58 ppm
pH	7.2	SO ₄ ²⁻	2.26 ppm-S
DOC	12.4 ppm-C	Cu ²⁺	8 ppb
NH ₄ ⁺	0.17 ppm-N	Zn ²⁺	24 ppb
NO ₂ ⁻ /NO ₃ ⁻	0.05 ppm-N	Fe	3,048 ppb
PO ₄ ³⁻	0.03 ppm-P	Na ⁺	4.28 ppm
TDN	0.75 ppm-N	K ⁺	0.91 ppm
TDP	0.12 ppm-P	Ca ²⁺	9.70 ppm
F ⁻	0.05 ppm	Mg ²⁺	1.68 ppm

Further experiments were conducted on Calgon GAC for all media and data was included and interpreted. While conducting these experiments, the simple synthetic stormwater should have had 0 ppb iron (Fe), but a mistake was made and the synthetic matrix had ~1,500 ppb Fe; the results were not comparable to the other sorbents. Complex synthetic stormwater with no iron in fact had 237 ppb Fe for soil, biochar, EarthLite™, and RemBind®. When this experiment was done for Calgon GAC, there was 0 ppb Fe as intended, so the results for GAC are again incomparable to the other sorbents. Experiments for soil, biochar, EarthLite™, and RemBind® in complex synthetic were retested to contain no iron so the results can be directly compared. Aside from those two sorbent media, all other stormwater media are directly comparable. Additional experiments were conducted to address these experimental inconsistencies. Due to this, results for Calgon GAC are separate from the others (Figure 11).

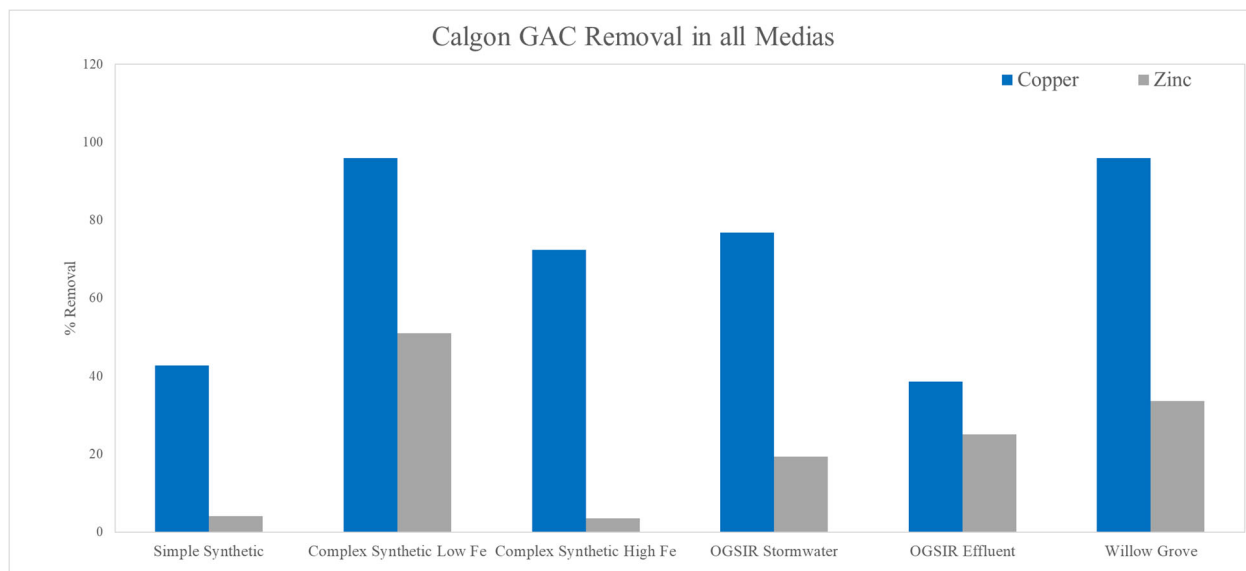


Figure 11: Copper and zinc percent removal for Calgon GAC in all stormwater media.

The OGSIR stormwater was fully characterized. Sorbent experiments and biofilm examinations were completed and data presented below. Column experiments were completed for sand, biochar/sand mixtures, and Calgon F400 GAC/sand mixtures for heavy metal removal from real stormwater in the presence and absence of biofilms.

SEM imaging showed that biofilms readily formed on biochar (Figure 12) and GAC (Figure 13) but less so on sand grains (Figure 14). In the absence of biofilms, biochar performed better than Calgon F400 (GAC) at removing zinc and copper from real stormwater (Figure 15-Figure 16, Table 6). Both of these sorbents performed significantly better than sand, which only removed modest amounts of zinc and copper (Figure 17). When biofilms were present, all three sorbents improved in heavy metal removal with the exception of biochar and copper, which decreased slightly from the abiotic experiments (Table 6, Figure 18-Figure 20).

In the absence of biofilms, biochar easily outperformed Calgon F400 (GAC); in the presence of biofilms, the two sorbents behaved similarly with Calgon F400 (GAC) performing a bit better.

The results of these studies indicated that the presence of biofilms will enhance heavy metal removal by these sorbents in the field. Additionally, the biotic columns suggest that the presence of biofilms may mute the difference between different carbon-based sorbents for removing heavy metals from stormwater.

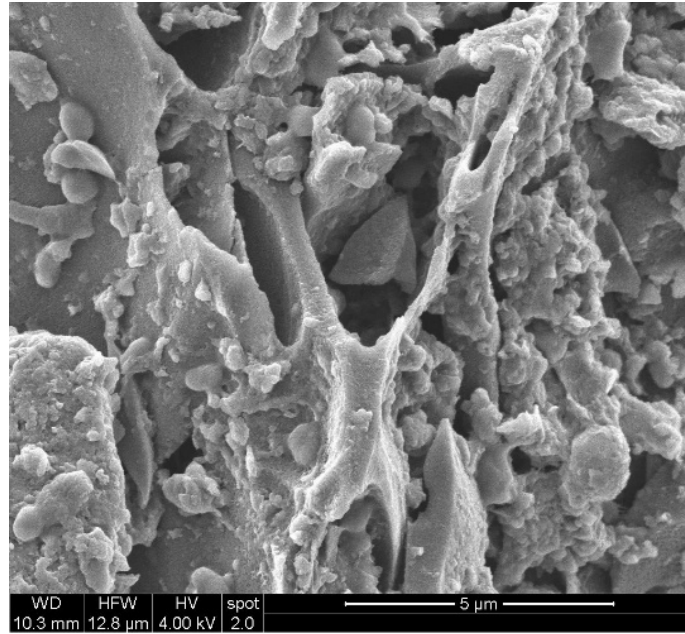


Figure 12: SEM image of biofilms on biochar.

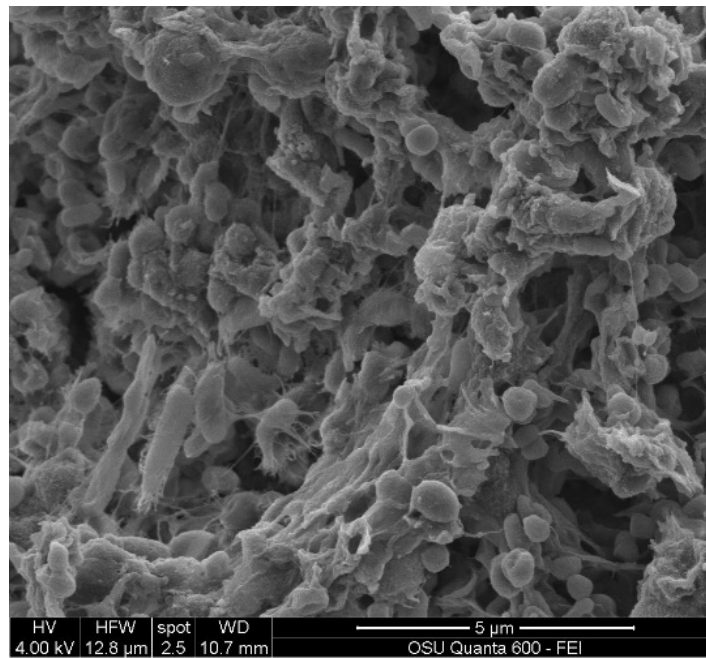


Figure 13: SEM image of biofilms on Calgon F400 (GAC).

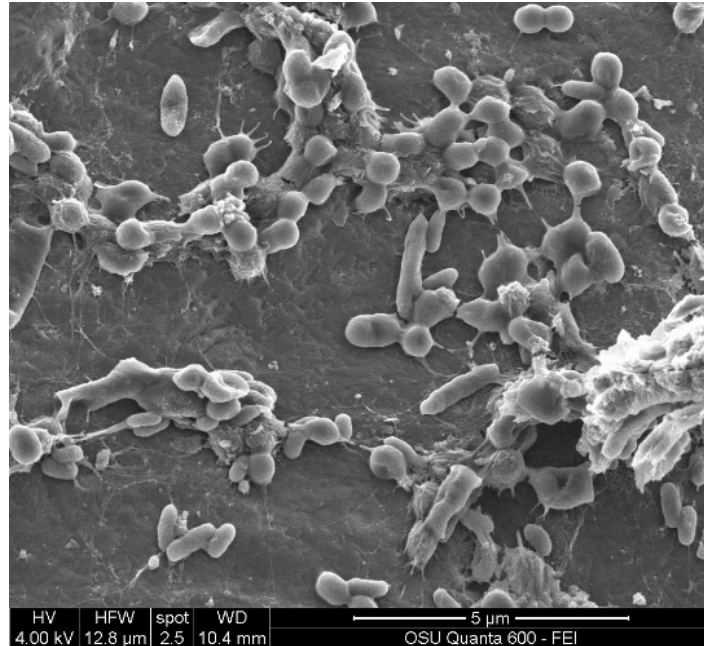


Figure 14: SEM image of biofilms on sand.

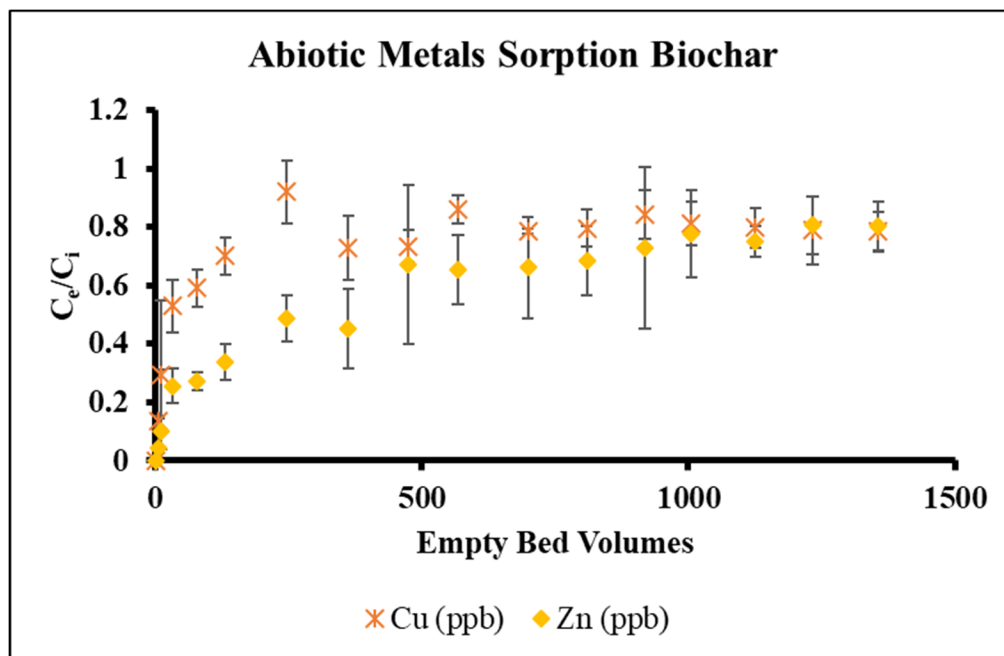


Figure 15: Copper and zinc adsorption by biochar columns without biofilms.
Error bars represent 95% confidence intervals from triplicate columns.

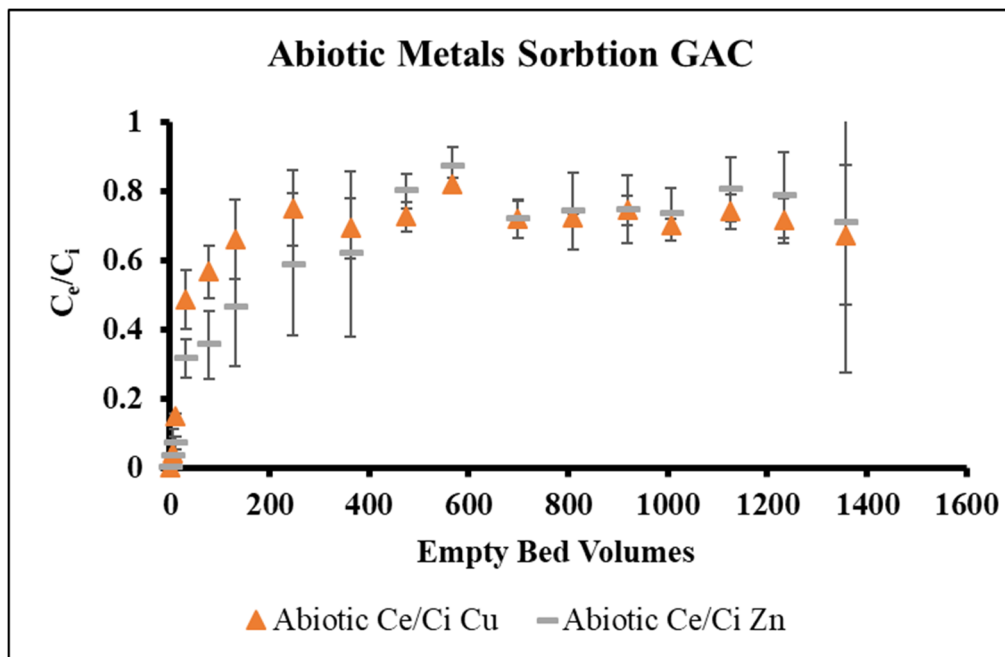


Figure 16: Copper and zinc adsorption by Calgon F400 (GAC) columns without biofilms. Error bars represent 95% confidence intervals from triplicate columns.

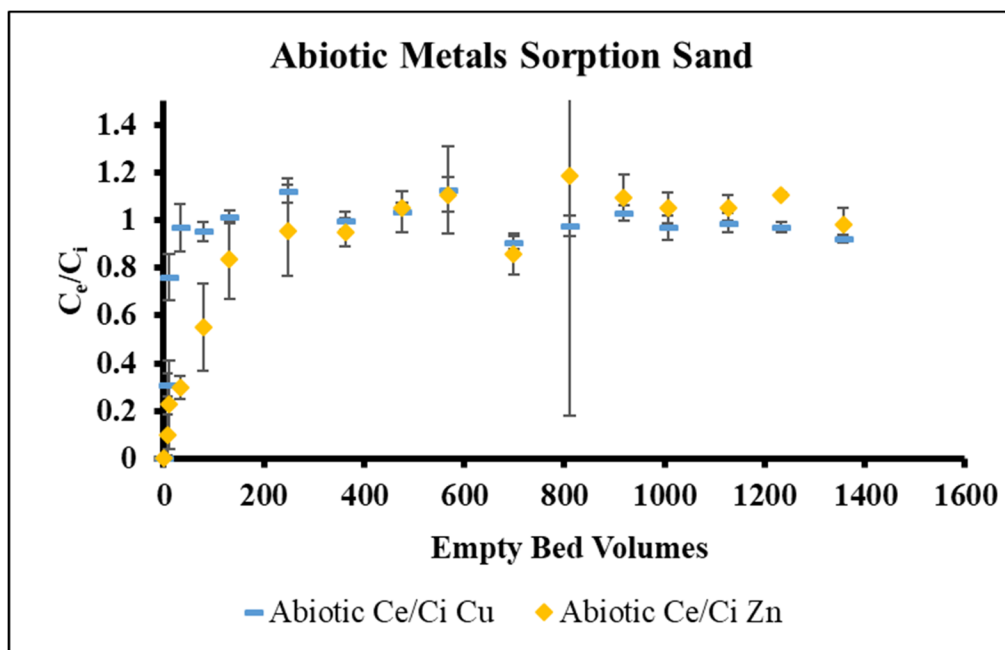


Figure 17: Copper and zinc adsorption by Calgon F400 (GAC) columns without biofilms. Error bars represent 95% confidence intervals from triplicate columns.

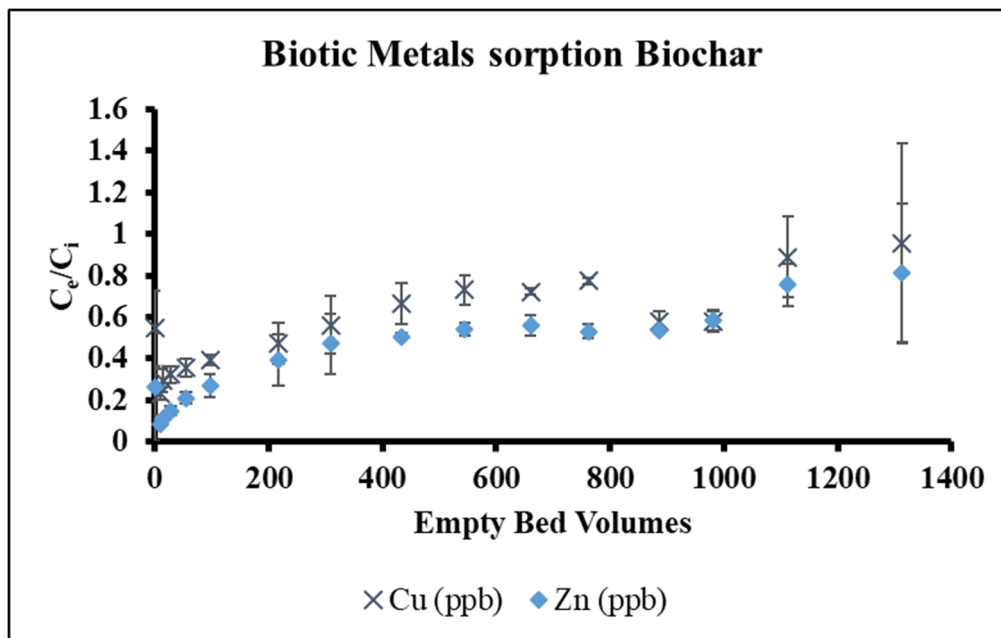


Figure 18: Copper and zinc adsorption by biochar columns containing biofilms enriched from stormwater.

Error bars represent 95% confidence intervals from triplicate columns.

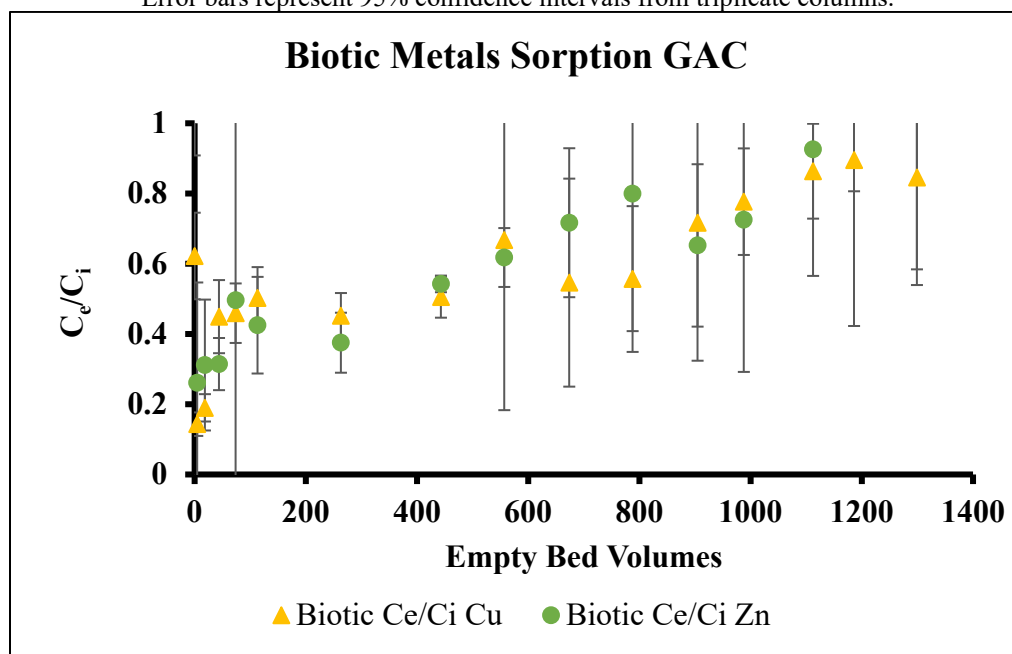


Figure 19: Copper and zinc adsorption by Calgon F400 (GAC) columns containing biofilms enriched from stormwater.

Error bars represent 95% confidence intervals from triplicate columns.

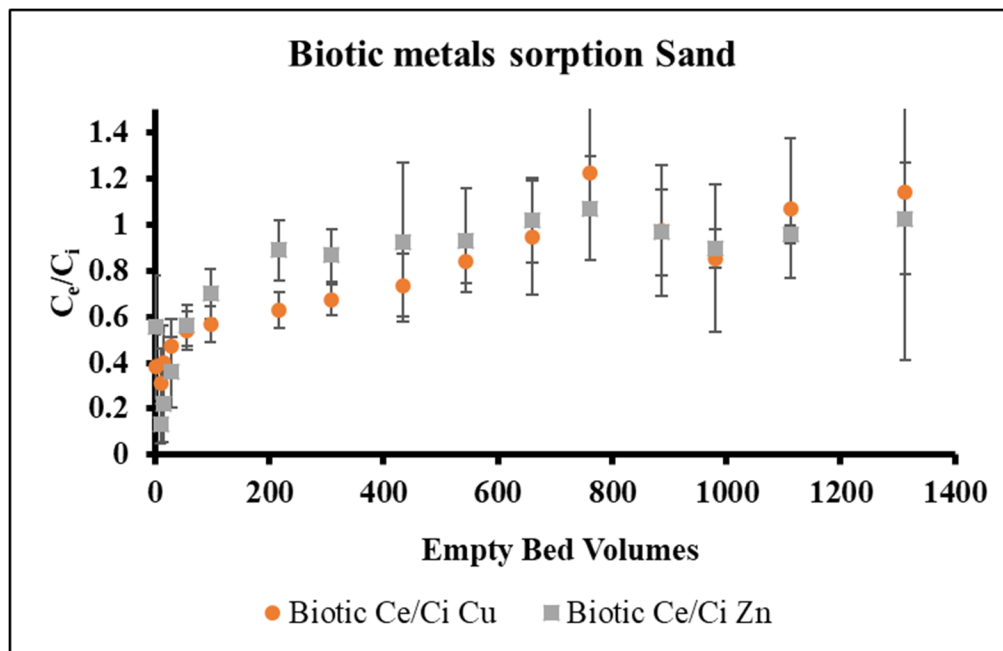


Figure 20: Copper and zinc adsorption by sand columns containing biofilms enriched from stormwater.

Error bars represent 95% confidence intervals from triplicate columns.

Table 6: Number of empty bed volumes required to reach an effluent concentration that is 50% of the influent concentration in rapid small scale columns treating heavy metal containing stormwater.

	Empty Bed Volumes to 50% Breakthrough			
	Abiotic		Biotic	
	Cu ²⁺	Zn ²⁺	Cu ²⁺	Zn ²⁺
Sand	8	45	99	49
Calgon F400 (GAC)	72	148	142	412
Biochar	150	216	127	374

When the experimental columns in Task 1.4 had reached 100% sorption capacity, the columns were fed a synthetic stormwater with no metals present. This tested the scenario of a storm with minimal metals coming into contact with a sorbent fully saturated with metals which would result in the greatest driving force for metals to desorb from the sorbent. In all cases, zinc desorbed to a greater extent than copper, and sorbents with biofilms released less zinc and copper than sorbents not containing biofilms (Figure 21-Figure 26). The results of these experiments demonstrate that zinc is more likely to desorb than copper from these sorbents and that biofilms help mitigate the release of these metals.

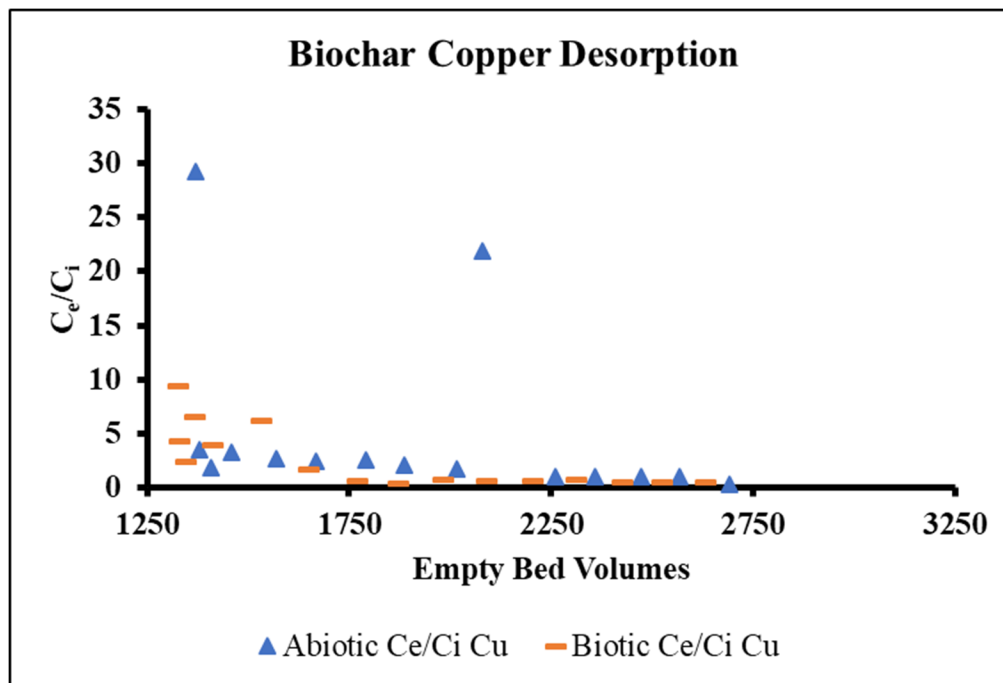


Figure 21: Copper desorption by from spent biochar columns in the presence or absence of biofilms enriched from stormwater.

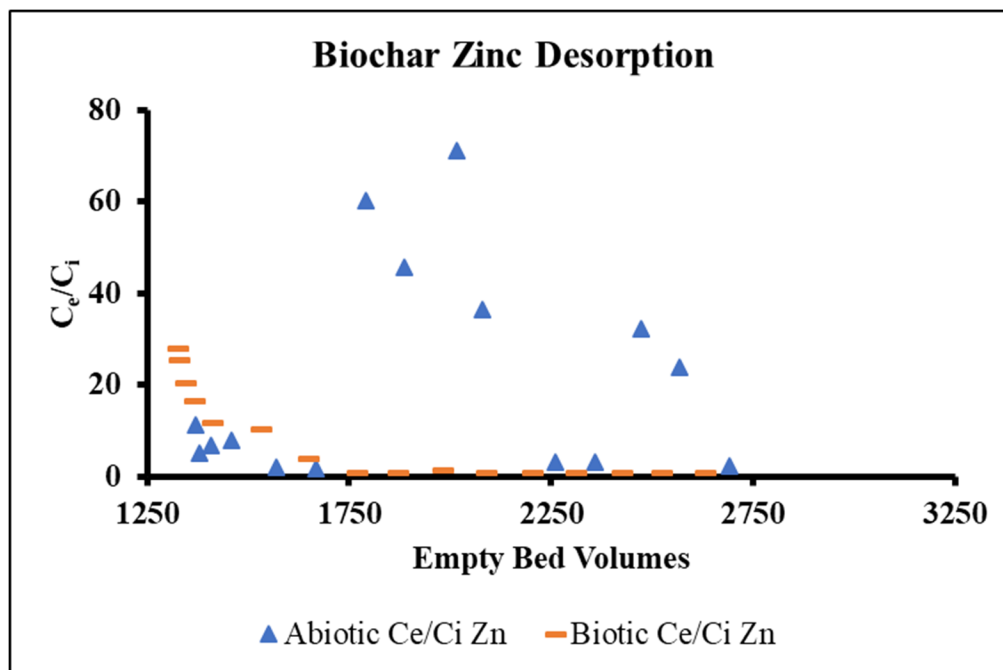


Figure 22: Zinc desorption by from spent biochar columns in the presence or absence of biofilms enriched from stormwater.

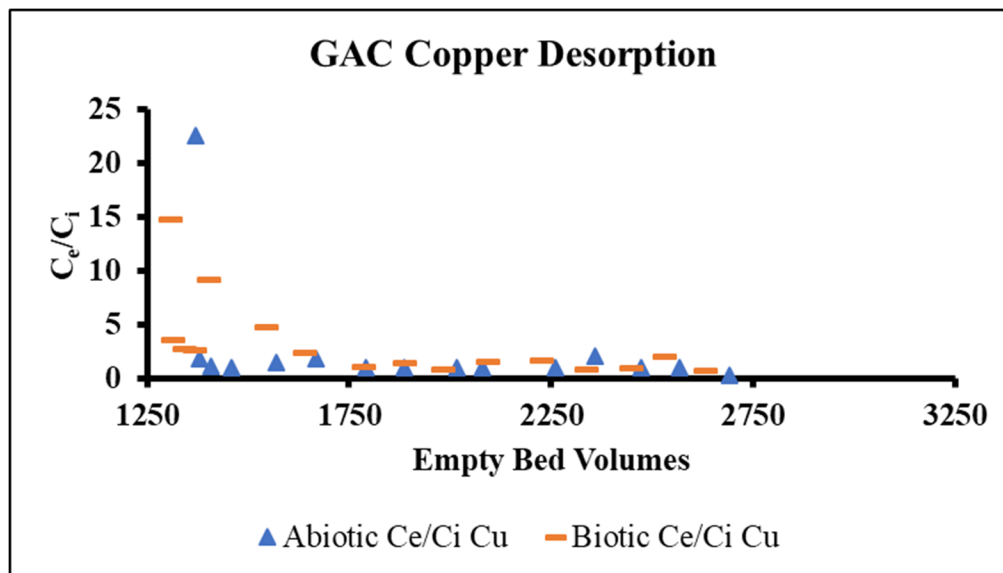


Figure 23: Copper desorption by from spent Calgon F400 (GAC) columns in the presence or absence of biofilms enriched from stormwater.

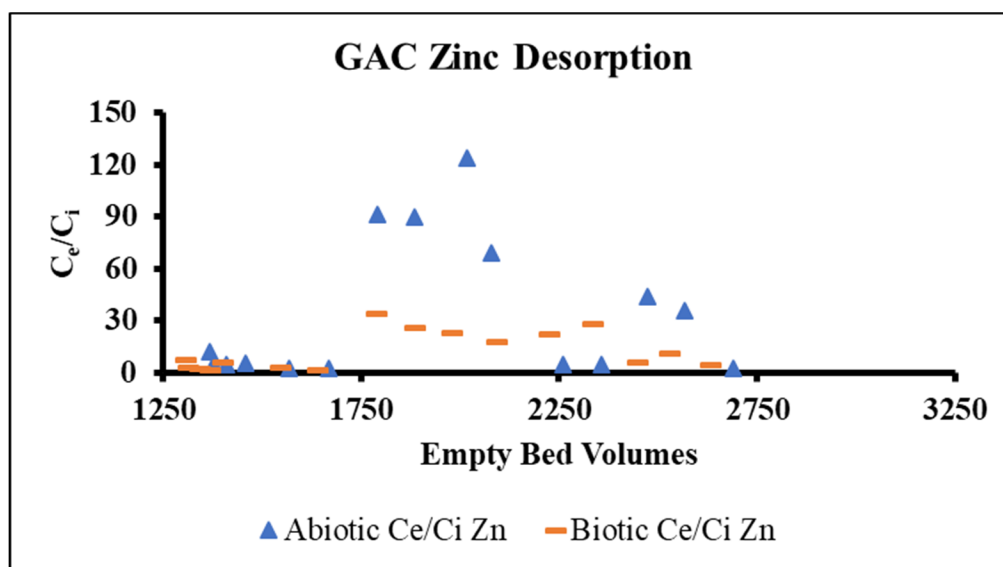


Figure 24: Zinc desorption by from spent Calgon F400 (GAC) columns in the presence or absence of biofilms enriched from stormwater.

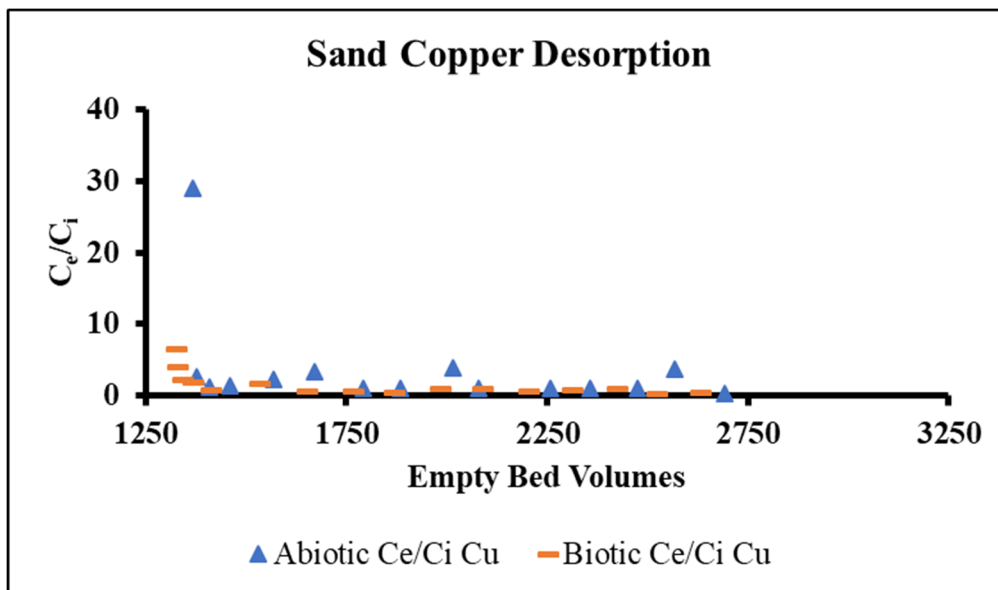


Figure 25: Copper desorption by from spent sand columns in the presence or absence of biofilms enriched from stormwater.

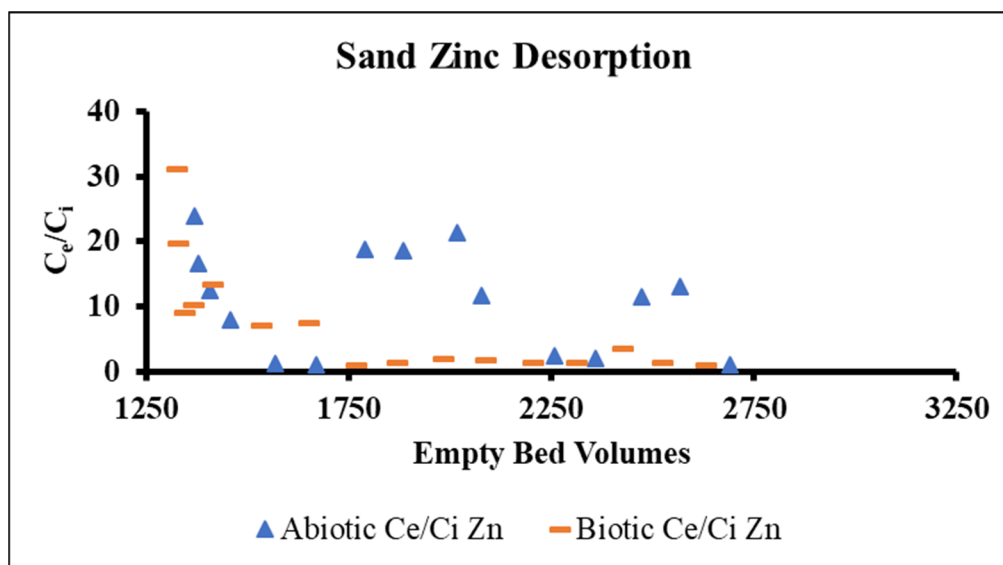


Figure 26: Zinc desorption by from spent sand columns in the presence or absence of biofilms enriched from stormwater.

Task 2

Copper results

Removal of copper represents an important treatment goal of stormwater remediation systems. Most plants tested in this study out-performed the soil-only control (“Soil_SW”) in terms of

removal of total copper. This copper is, of course, associated largely with particulate matter which is removed from stormwater by simple physical capture. Particles laden with metals such as copper settle out of solution as the water slows down and gradually infiltrates down through the soil column.

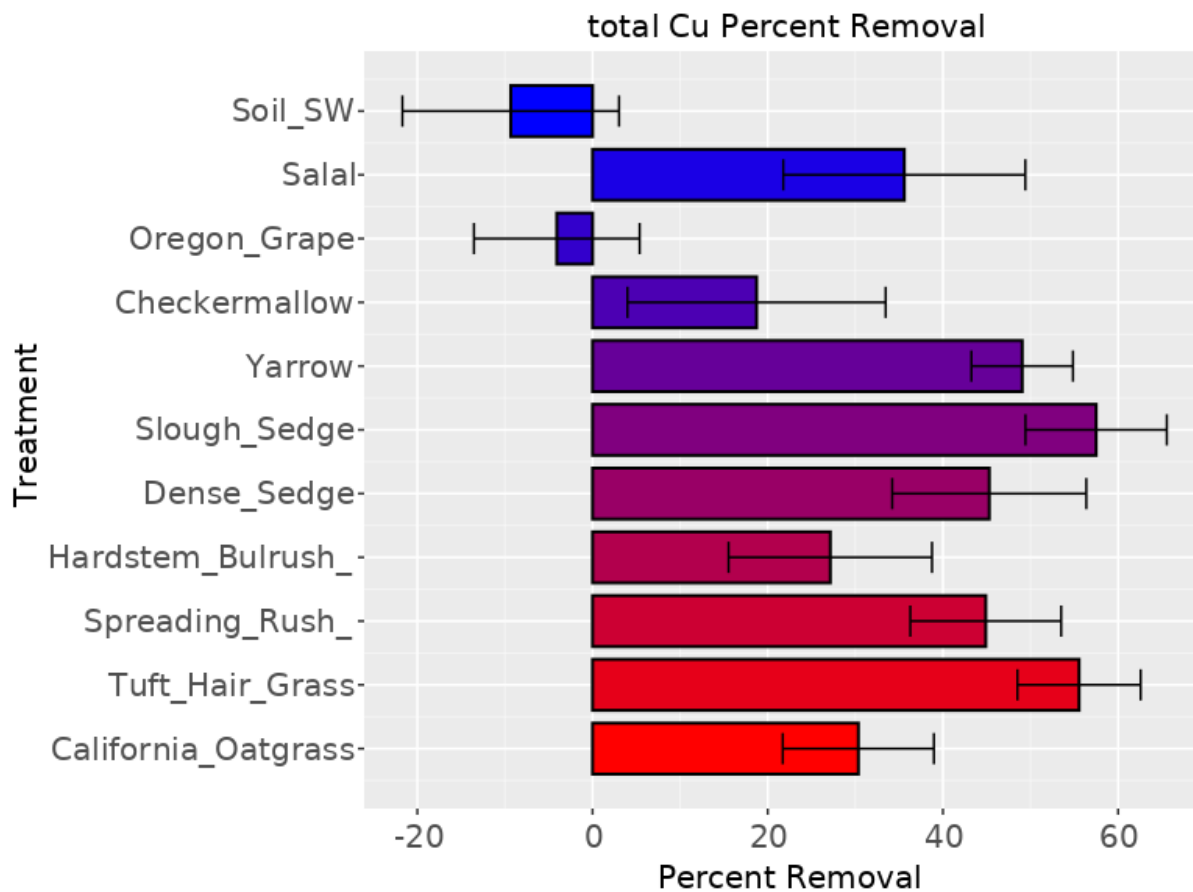


Figure 27: Total Copper Removal Efficiency (Soil SW is the soil only control receiving stormwater).

Error bars represent 95% confidence intervals

Oregon grape performed particularly poorly and was only plant not to achieve a net capture of copper. The best performers were tuft hair grass and slough sedge.

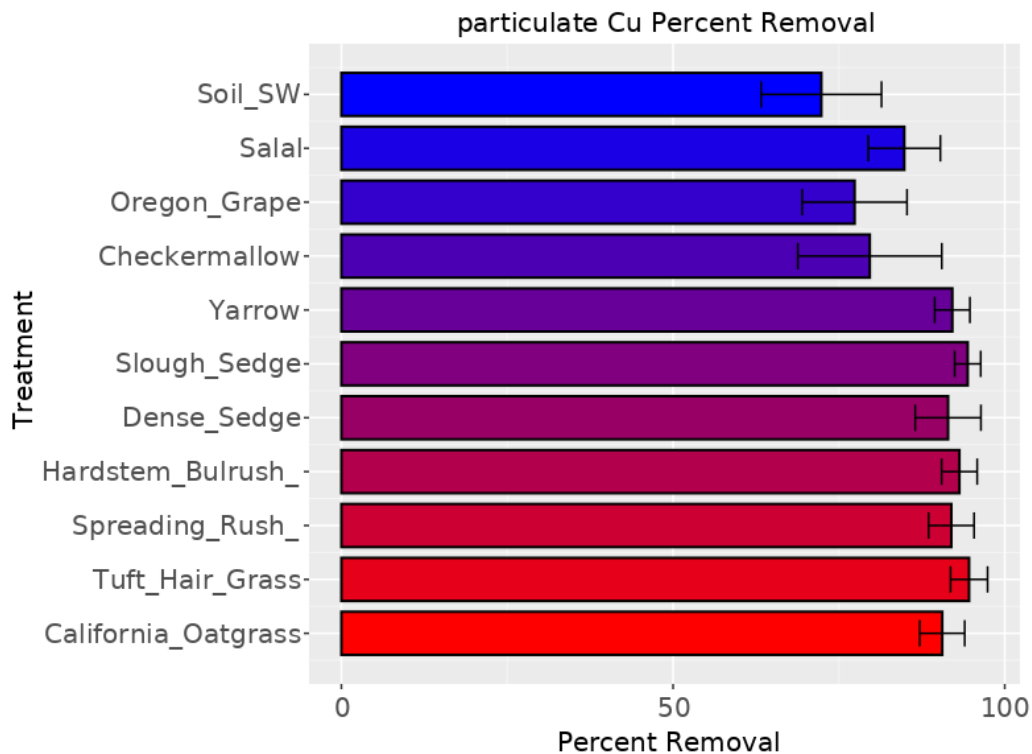


Figure 28: Percent Removal of Particulate Copper.
Error bars represent 95% confidence intervals

Significant removal of particle associated copper is achieved by all plants studied, with most achieving 80-90% removal, above the ~70% removal achieved by the soil. Particulate copper is defined as:

$$\text{Total Copper} - \text{Dissolved Copper} = \text{Particulate Copper}$$

(Equation 2)

The worst performers among the plants all come from the dicotyledons (salal, Oregon grape, and checkermallow) with yarrow being the lone member of this group to remove particulate copper at the same level as the grasses, rushes, and sedges (monocotyledons).

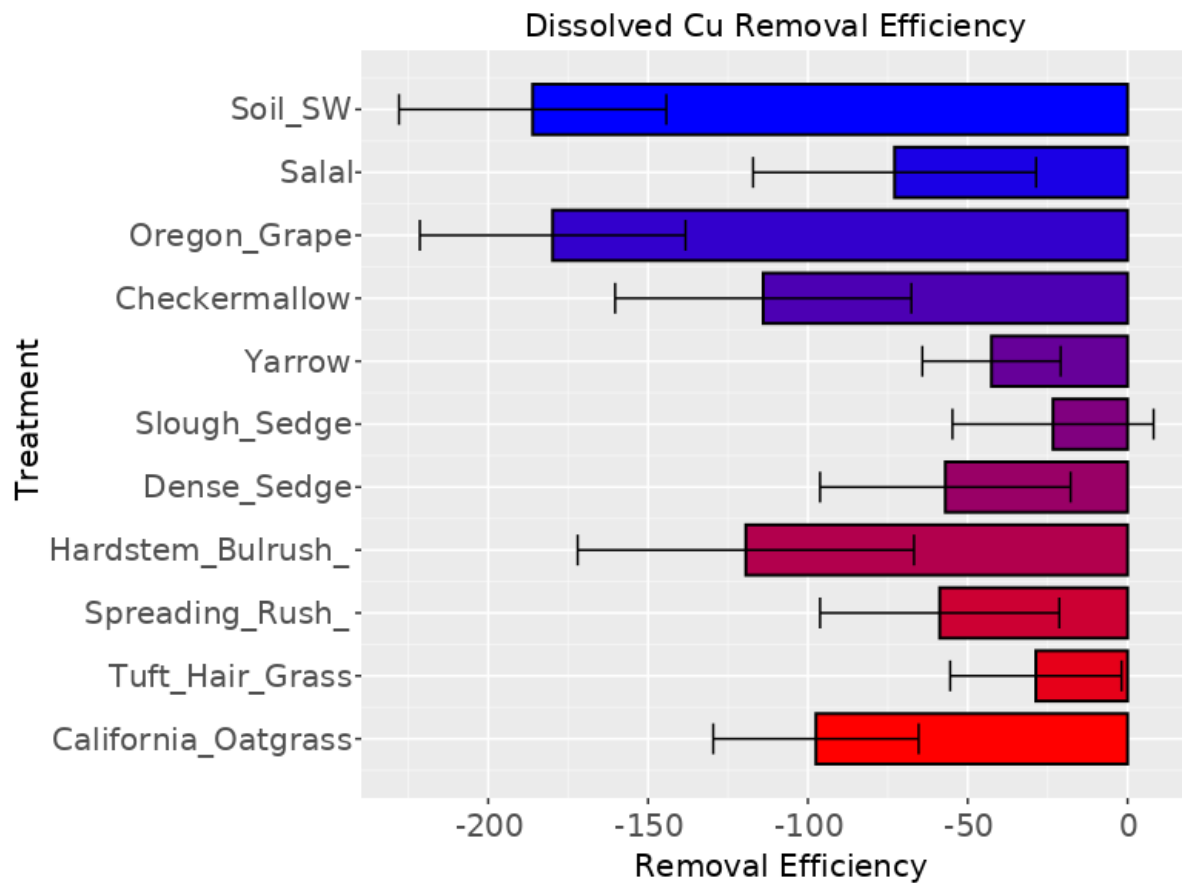


Figure 29: Dissolved Copper Removal Efficiency.
Error bars represent 95% confidence intervals

Dissolved copper removal efficiency is not clearly related to the plant's phylogeny (though it appears to be for particulate removal; Figure 29). All plants perform quite poorly, though some are extremely poor while others are merely poor.

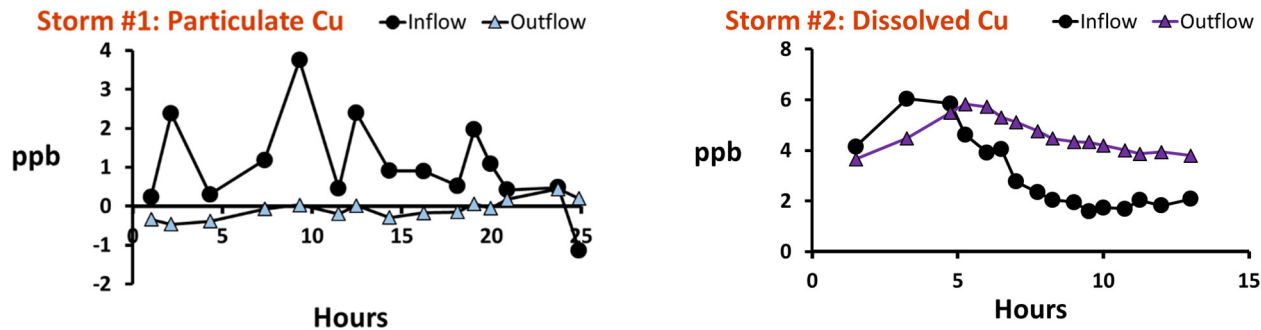


Figure 30: Dissolved and Particulate Copper influent vs. effluent in 2 storms at the OGSIR field site.

These disparities between dissolved and particulate copper treatment are consistent with results observed both at our field site and many others (Figure 30). The high copper content of the composts that are used in planting and building these LIDs (similar soil was used in this experiment) are a significant source for dissolved copper, so many LIDs are actually net exporters of dissolved copper, at least over the short term.

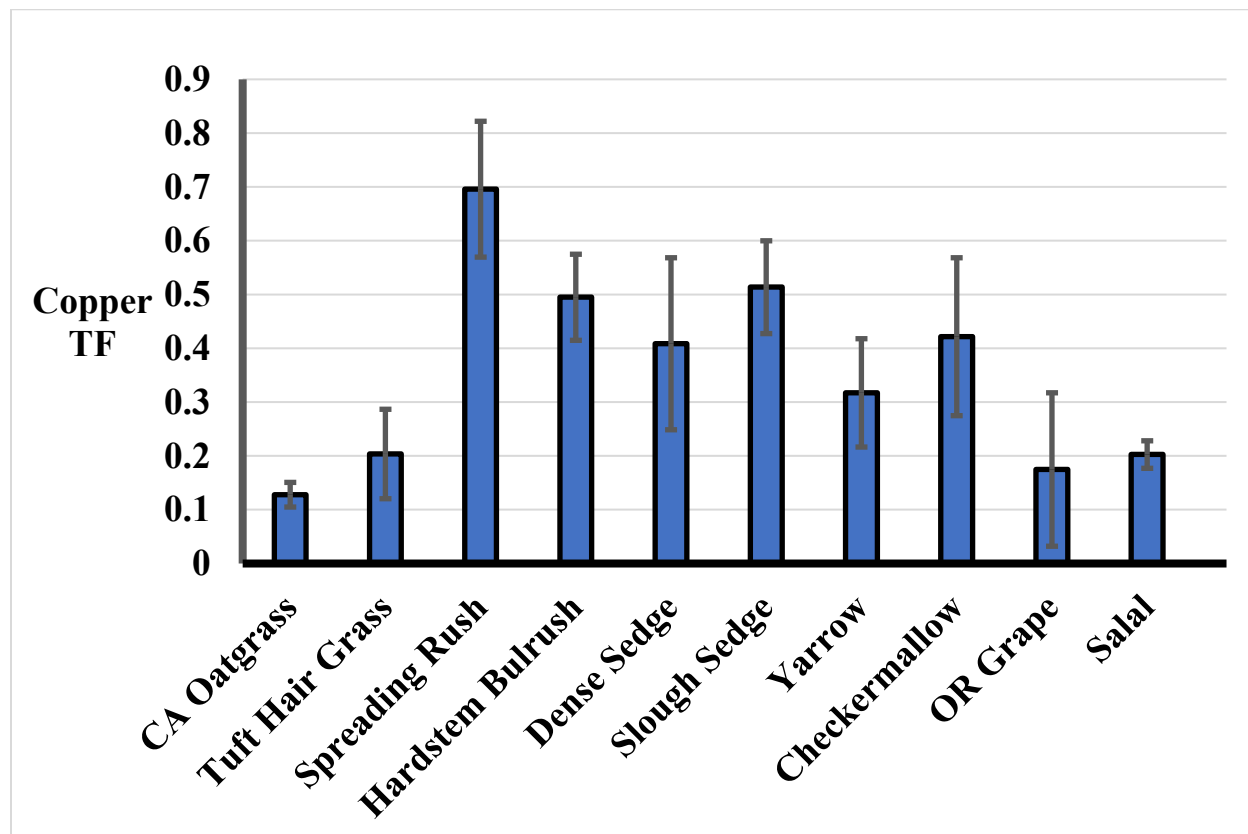


Figure 31: Copper translocation factor. The concentration in the stems and leaves divided by the concentration in the roots. Error bars represent 95% confidence intervals.

Copper translocation did not exceed unity for any treatment (Figure 31), meaning no plant succeeding in concentrating more copper (per mass plant tissue) in the above ground parts of the plant as compared with the roots. It was expected that high translocation would allow for remediation by pruning plants, but copper remains a very difficult metal to treat in stormwater. The rushes and sedges were most successful in concentrating copper, suggesting their preferential inclusion in various LIDs.

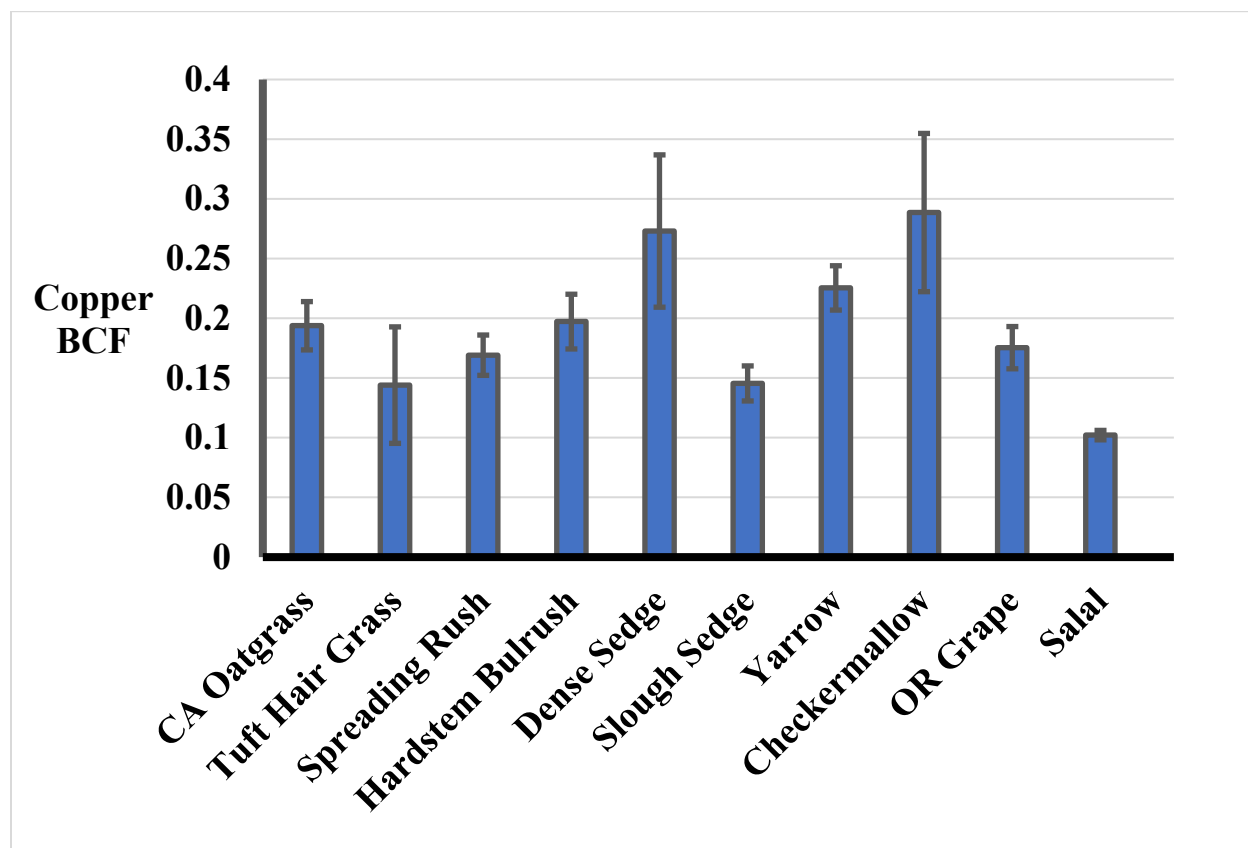


Figure 32: Copper bioconcentration factor. Error bars represent 95% intervals. The concentration in the plant divided by the concentration in the soil.

No plants achieved a bioconcentration factor above unity for copper, though soil concentrations of copper are very high in such systems (Figure 32). The best performances were exhibited by dense sedge and checkermallow.

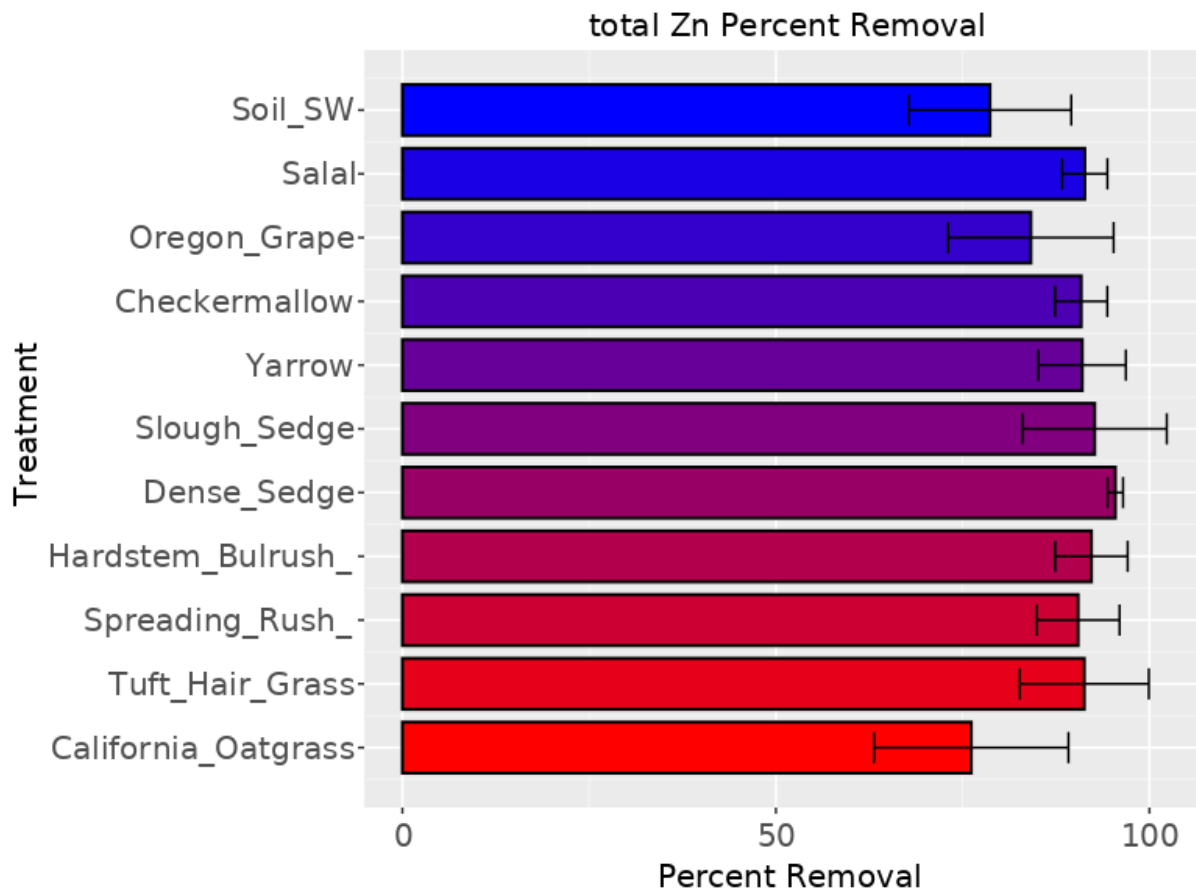


Figure 33: Total Zinc Removal.
Error bars represent 95% confidence intervals

Total zinc removal was considerable across all treatments, with each recording over 75% removal (Figure 33). The worst performers were the soil-only control and California oatgrass. The best total zinc removal is attributed to dense sedge, slough sedge, and salal.

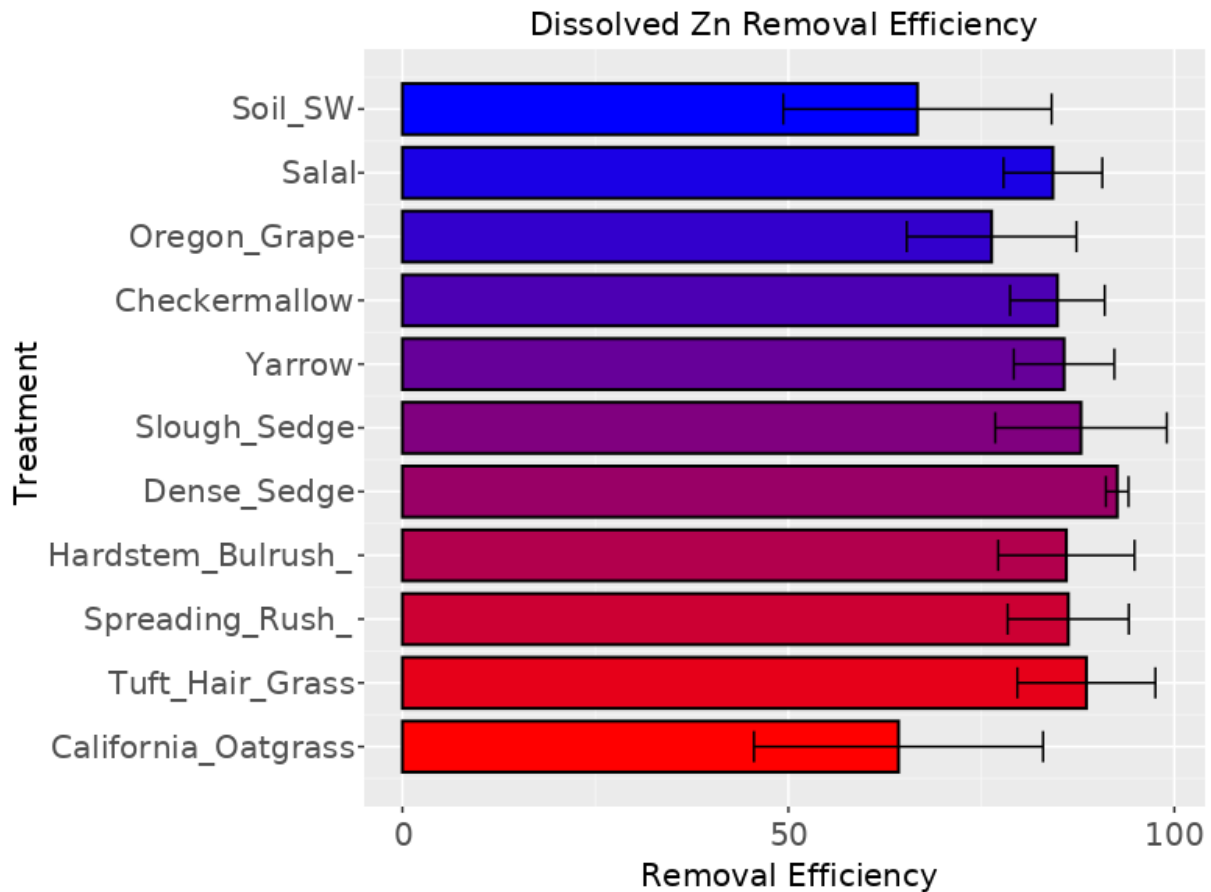


Figure 34: Dissolved zinc removal efficiency.
Error bars represent 95% confidence intervals

Removal of dissolved zinc largely reflected the performance of total zinc removal (Figure 34). California oatgrass and the soil-only control were the worst performers; dense sedge, slough sedge, and salal performed the best, as above.

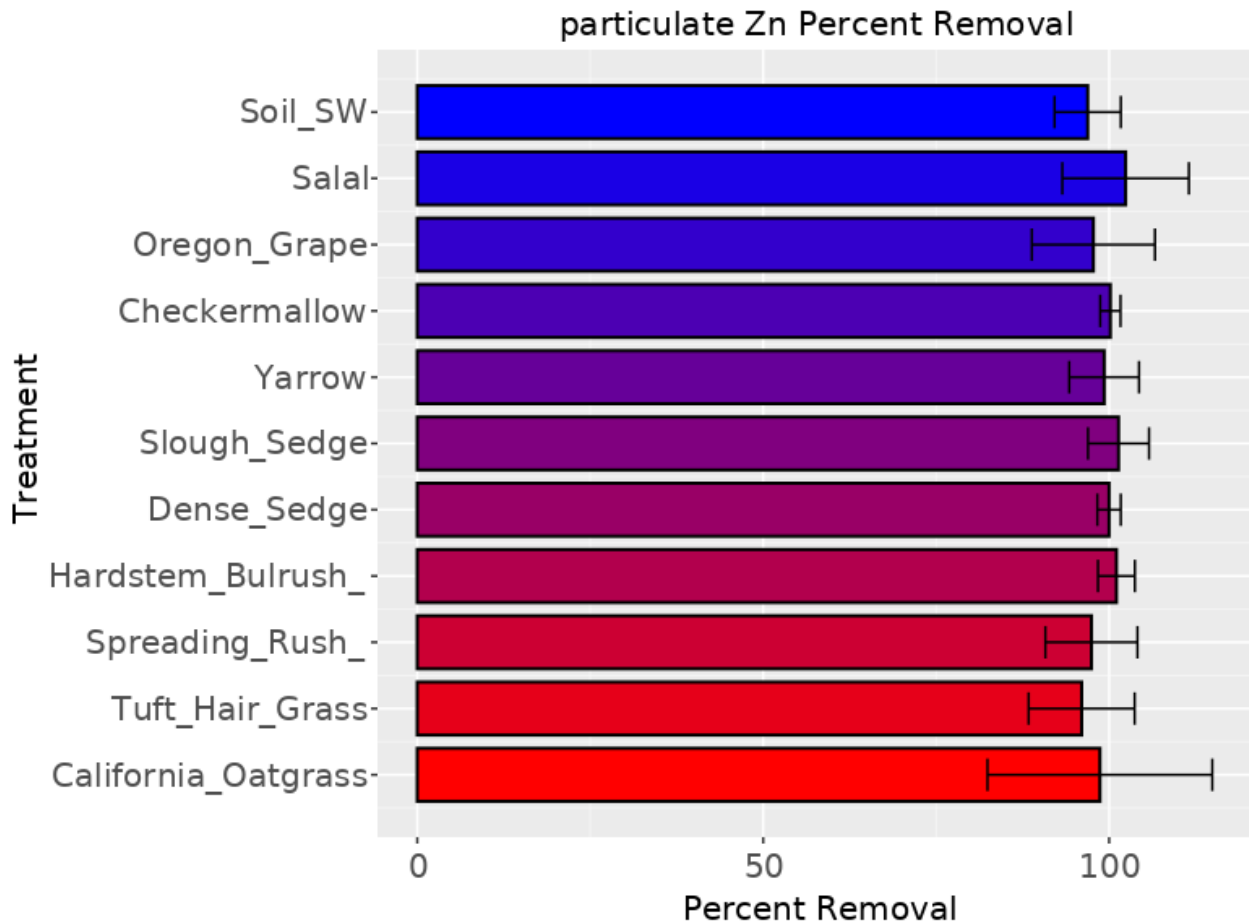


Figure 35: Removal Efficiency of Particulate Zinc.
Error bars represent 95% confidence intervals

Removal of particle-associated zinc approached 100% across all treatments and is not clearly differentiated among these treatments and presented no significant effect (Figure 35). The California oatgrass error bars reflected a much larger range than most in this category and call into question the true value of that treatment result, but most ranges on these confidence intervals are narrow enough to be confident in the high-level of treatment.

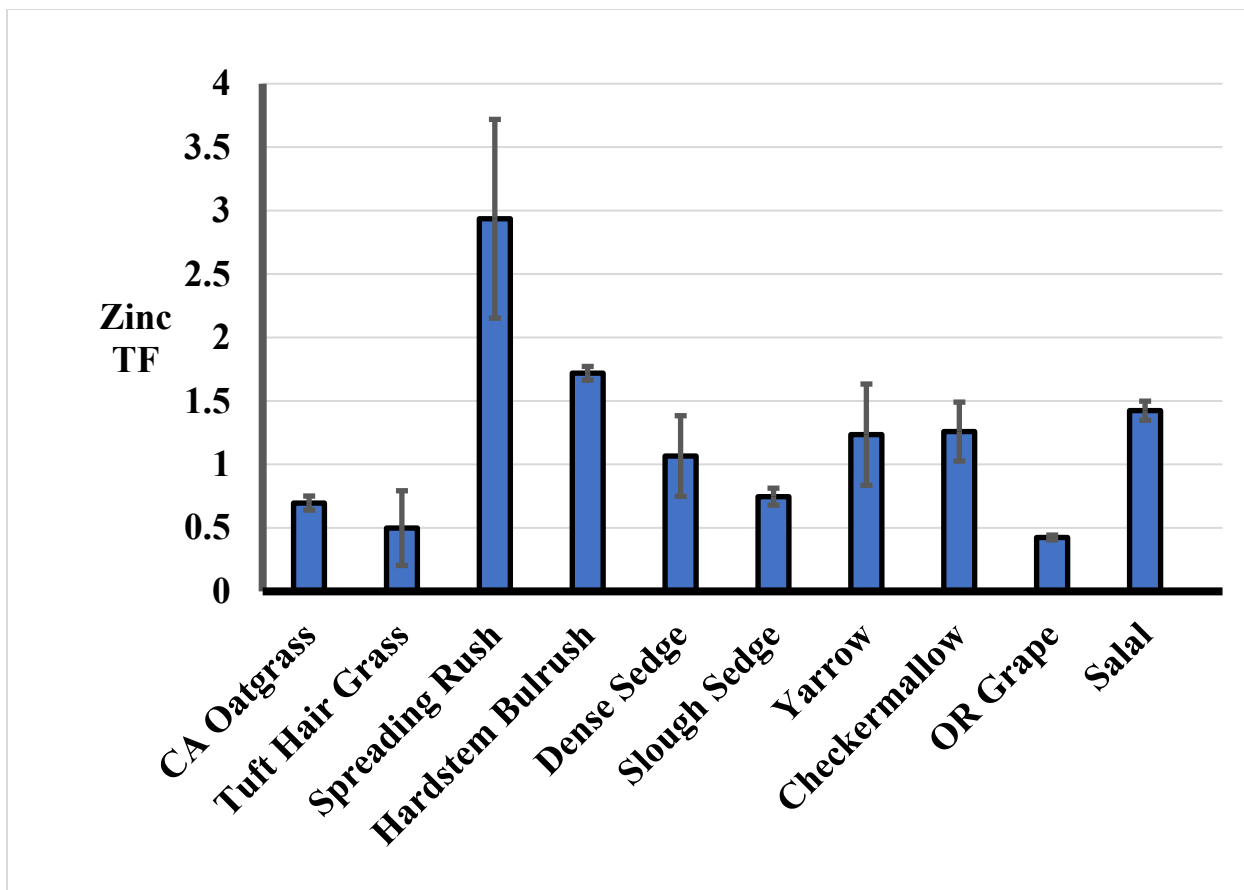


Figure 36: Zinc translocation factor. Error bars represent 95% confidence intervals. The concentration in the stems and leaves divided by the concentration in the roots.

The best plant for translocating zinc from the roots to the shoots was spreading rush, achieving a concentration in the leaves three times greater than in the roots. This suggests that sites with significant zinc loading rates may be better ameliorated in the long term by a spreading rush planting and pruning strategy.

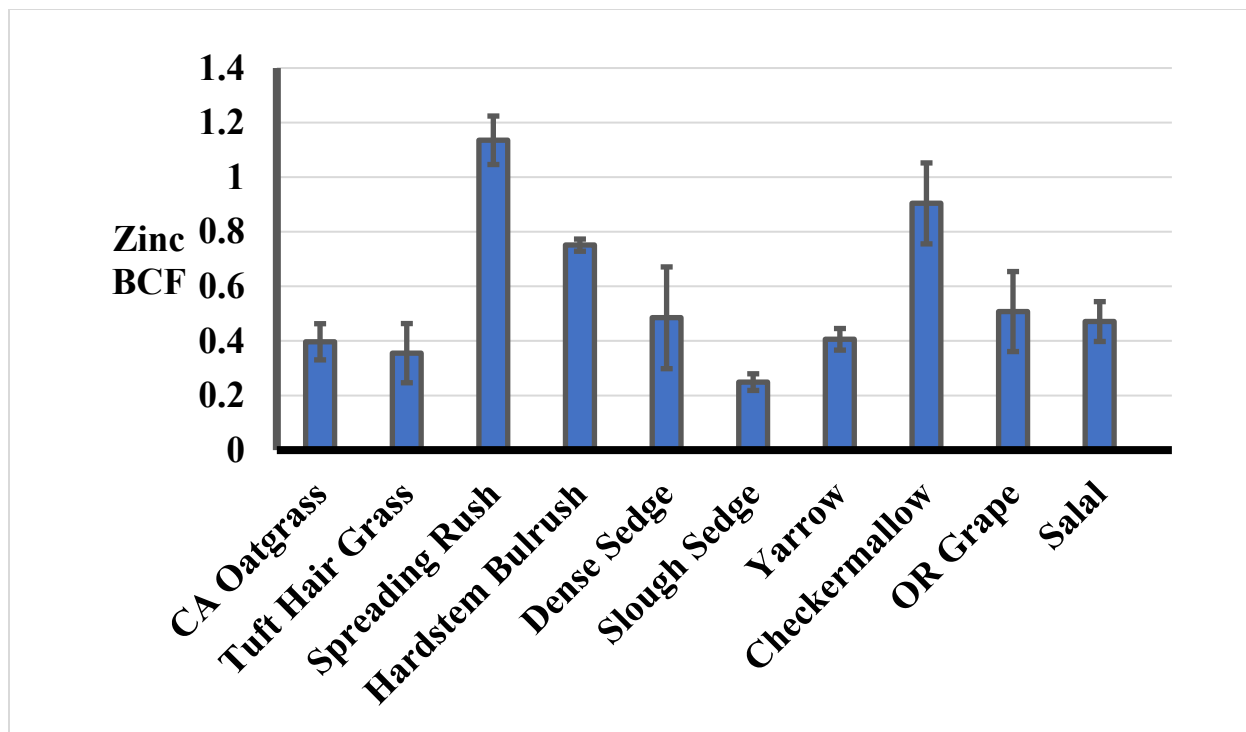


Figure 37: Zinc bioconcentration factor. Error bars represent 95% confidence intervals. The concentration in the plant divided by the concentration in the soil.

Both spreading rush and checkermallow were able to accumulate around the same concentration of zinc in their tissue as measured in the soil. No hyperaccumulation was observed and thus bioconcentration of zinc is not the major component of the total phytoremediation provided by plants in such systems.

PFAS Results and Discussion

Mass Balance

The sum-total PFAS (Σ PFAS) recovered in the whole plant and soil-only control fell within 70 and 130% for eight out of ten plants and the soil-only control (Figure 38). Individual PFAS also fell within 70 and 130% recovery, except for PFOA, PFDA, and PFBS, which were ~65% recovery. The most notable exception is the two perfluoroalkyl sulfonamides included, FHxSA and FOSA, which consistently fell below 40% recovery. Most of the Σ PFAS mass for each treatment was found in the soil, followed by the effluent, leaves, weeds, roots, and finally stems, which accounted for an insignificant fraction of the total mass (< 1%).

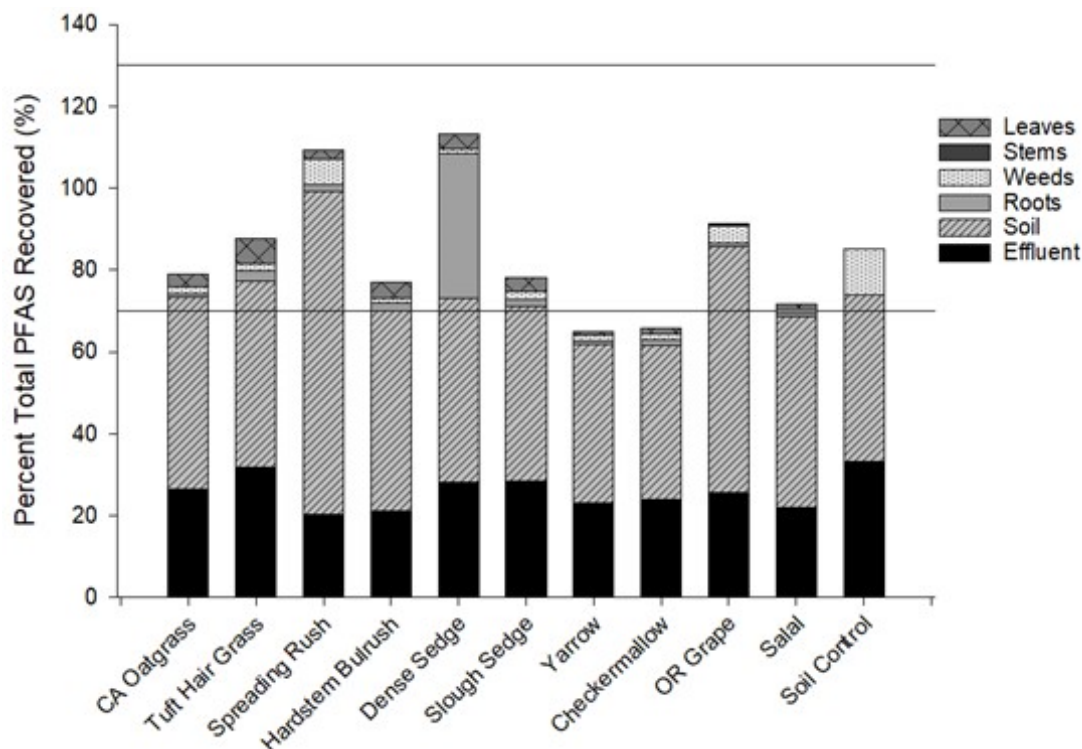


Figure 38: Mass Balance on PFAS recovered

In general, roots accounted for less than 2% of PFAS mass, with the exception being dense sedge with 36% PFAS found in the roots. Dense sedge had a moderate average root mass compared to the other plant treatments (23.6 ± 0.7 g) but some of the highest concentrations of most PFAS, particularly of longer-chain PFAS. For example, dense sedge had the second highest PFNA root concentration of 6900 ± 1300 ng/kg. The combination of high root mass and high PFAS concentration resulted in a large fraction of PFAS mass contained in dense sedge roots. For comparison, tuft hair grass had the highest root concentration of PFNA, but one of the lowest average root masses resulting in 3.5% of PFNA contained in tuft hair grass roots versus the 35.1% of PFNA contained in dense sedge roots.

The percent of PFAS found in weeds varies among treatments, with the greatest percent of PFAS in leaves found in the soil-only control. It's possible that PFAS were partially taken up by weeds; however, there is not sufficient evidence to support that weeds are more efficient at taking up PFAS than the other plant treatments. Future work should focus on uptake of PFAS by weeds, as they are environmentally relevant and could potentially contribute to PFAS removal in the environment.

Branched vs. Linear PFOS

The average percent linear PFOS isomer in plants was greatest in soil ($84 \pm 1\%$) compared to roots ($82 \pm 1\%$), stems ($77 \pm 7\%$), leaves ($76 \pm 2\%$), influent ($74 \pm 2\%$), and effluent ($57 \pm 2\%$). Enrichment of the linear PFOS isomer is observed in the soil, roots, stems, and leaves relative to influent, which is consistent with previous findings that plants all plant components preferentially take up linear PFOS compared to branched PFOS due to the decreased

lipophilicity of branched PFOS. The percent linear of PFOS in roots falls within the range of 80-83% previously observed, while percent linear in leaves falls slightly below the range of 78-85%.

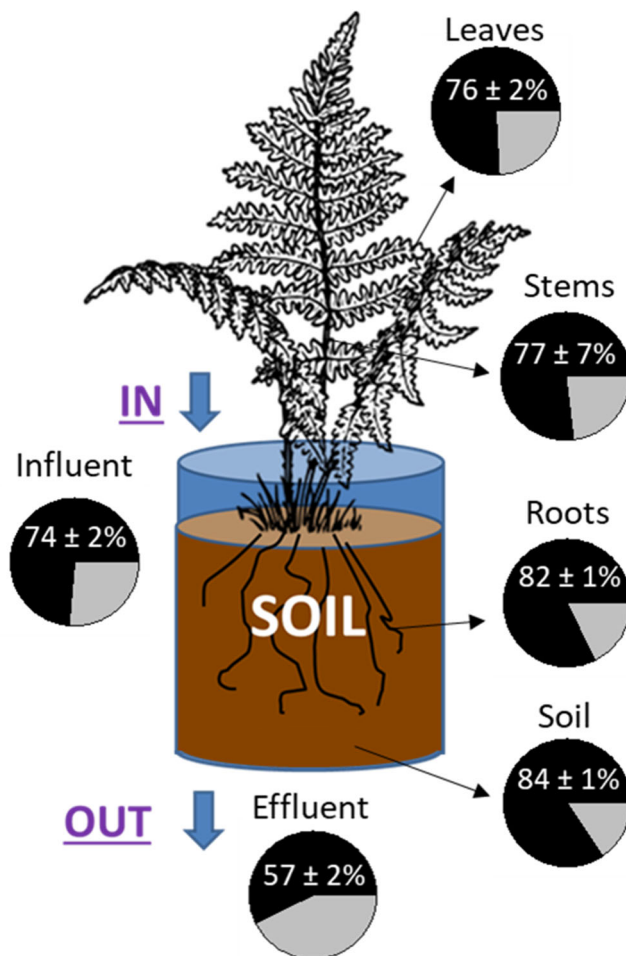


Figure 39: Distribution of branched vs linear PFOS within plant and soil compartments. Percentages represent the average percent linear of all plants with a 95% CI.

There were few significant differences in percent linear PFOS isomer in leaves, stems, soil, and effluent among plant groups. Roots however, demonstrated the most variation in percent linear among plant groups. Rushes, sedges, and stemless dicots all had significantly greater percent linear in the roots than grasses and stemmed dicots. The percent linear PFOS isomer in roots showed a relatively high correlation ($R^2 = 0.72$) with the average root mass, indicating a preference for root adsorption by linear PFOS. Although not measured, root surface area would also likely be an important parameter for future studies, but was not within the scope of the current study.

Bioconcentration Factor (BCF)

The averaged PFAS BCF among groups of plants from greatest to lowest was: stemless dicots, grasses, sedges, rushes, and stemmed dicots. Both grasses and stemless dicots had significantly

greater BCFs than stemmed dicots, and stemless dicots also had significantly higher BCFs as compared to rushes. Among stemless dicots, eleven out of thirteen PFAS gave BCFs of greater than one, indicating that they bioaccumulate. Out of the eleven PFAS, PFBA, PFDA, PFBA, PFPeS, and FOSA gave BCF values greater than ten, indicating that they are hyper-accumulative in plants.

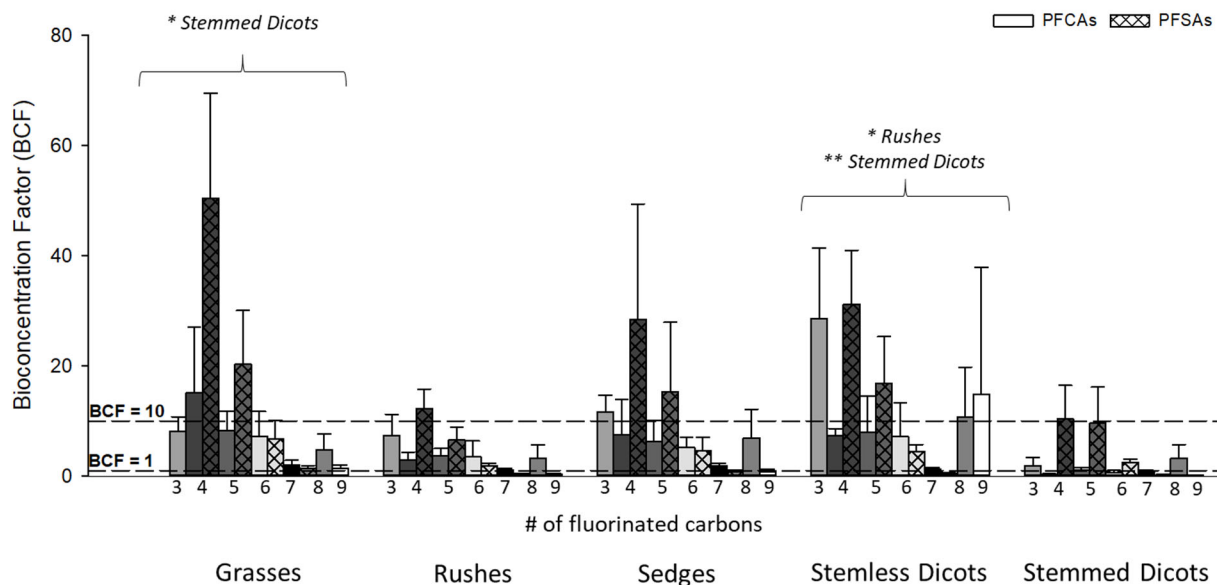


Figure 40: Bioconcentration factors of individual PFAS among grasses, rushes, sedges, stemless dicots, and stemmed dicots. Error bars represent standard deviation.

*: average PFAS BCF is significantly greater than other plant group with a $p < 0.05$;

***: average PFAS BCF is significantly greater than other plant group with a $p < 0.01$.

There did not appear to be a trend in BCF values among plant classes (e.g., monocots and dicots), indicating that plant class was independent of PFAS uptake. Within monocots, leaf structure was a possible explanation for the varying BCFs. For instance, grasses demonstrated the greatest BCFs across most PFAS compared to rushes and sedges. Grasses typically have flat, bladed leaves resulting in increased surface area to volume ratio relative to rushes and sedges, which have structured stems. This may lead to higher transpiration in the grasses.

Stemmed dicots had the lowest average PFAS BCF of 2.45, with the lowest individual PFAS BCFs for nine out of thirteen PFAS. A previous study reported low PFAS concentrations in the woody components of plants, which was consistent with the findings in the current study that demonstrated $<1\%$ PFAS mass in woody stems. Given these results, it was likely that the woody stems prevented transport of PFAS from the roots into the leaves, leading to low BCFs in stemmed dicots.

The only PFAS that consistently have BCFs of greater than one among all plant groups were PFBA, PFBS, and PFPeS, which was consistent with reports that shorter-chain PFAS are more bioaccumulative than longer-chain PFAS. Given the same number of fluorinated carbons, the difference in BCF values between PFCAs and PFSA was not constant across the range of

fluorinated chain lengths. For example, shorter-chain PFASs have greater BCFs than shorter chain PFCAs (e.g. PFBS vs. PFPeA, which both have three fluorinated carbons). However, as chain length increased, the difference between PFCAs and PFASs with the same number of fluorinated carbons became less apparent (e.g., PFHpA vs. PFHxS which both have six fluorinated carbons).

Mass Accumulation Factor (MAF)

An additional way to evaluate remediation potential of plants was through the total mass of PFAS in the leaves relative to the mass of PFAS in soil. Using this method, grasses, sedges, and stemless dicots were still the three plant groups with the greatest PFAS. However, while stemless dicots had the highest BCFs followed by grasses and sedges, grasses had the highest MAFs followed by sedges and stemless dicots.

From a remediation perspective, MAF is a valuable parameter to consider because it factors in both the concentration in the plant as well as the total mass of the plant. For example, a stemless dicot might appear to be the most efficient plant at removing PFAS based on BCF, but grasses tend to grow faster. In the case of this study, grasses had approximately four times the leaf mass as stemless dicots which results in a greater total PFAS mass removed. This comes with the caveat that a plant with a low BCF but a high MAF means more mass to dispose of when the treatment has run its course. Thus, the ideal candidate for PFAS removal would be a plant with a high BCF and high MAF, such as grasses.

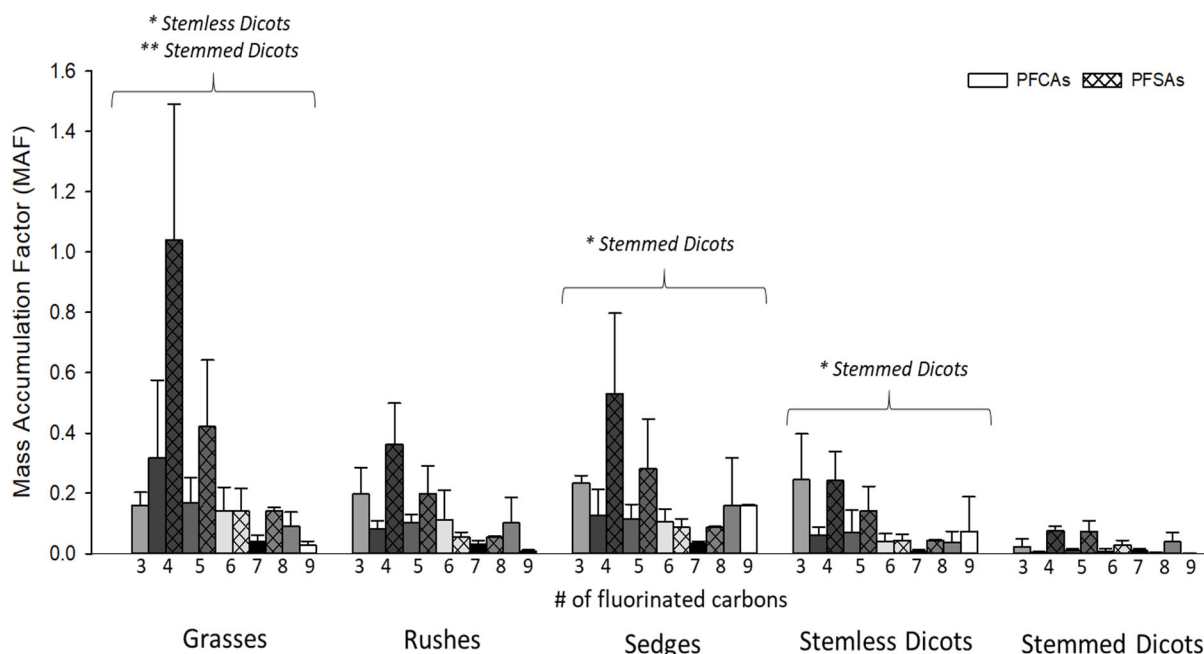


Figure 41: Mass accumulation factors for individual PFAS among grasses, sedges, stemless dicots, and stemmed dicots. Error bars represent standard deviation.

‘*’: average PFAS BCF is significantly greater than other plant group with a p < 0.05;

‘***’: average PFAS BCF is significantly greater than other plant group with a p < 0.01.

Translocation Factor (TF)

In general, stemless dicots have significantly greater TFs for PFAS than all other plant groups, followed by rushes and sedges. Within a homologous series, TFs decrease with increasing chain length. It is well established that the Casparian strip is a barrier for apoplastic transport and is easier for shorter-chain PFAS to overcome, resulting in greater translocation of short-chain homologs relative to long-chains. Given the same number of fluorinated carbons, PFCAs tend to have greater TFs than PFSA, although this is inconsistent among plant groups. Additionally, while FHxSA and FOSA are poor accumulators with BCFs < 1, they appear to be more efficient at translocation than PFCAs and PFSA with the same number of fluorinated carbons.

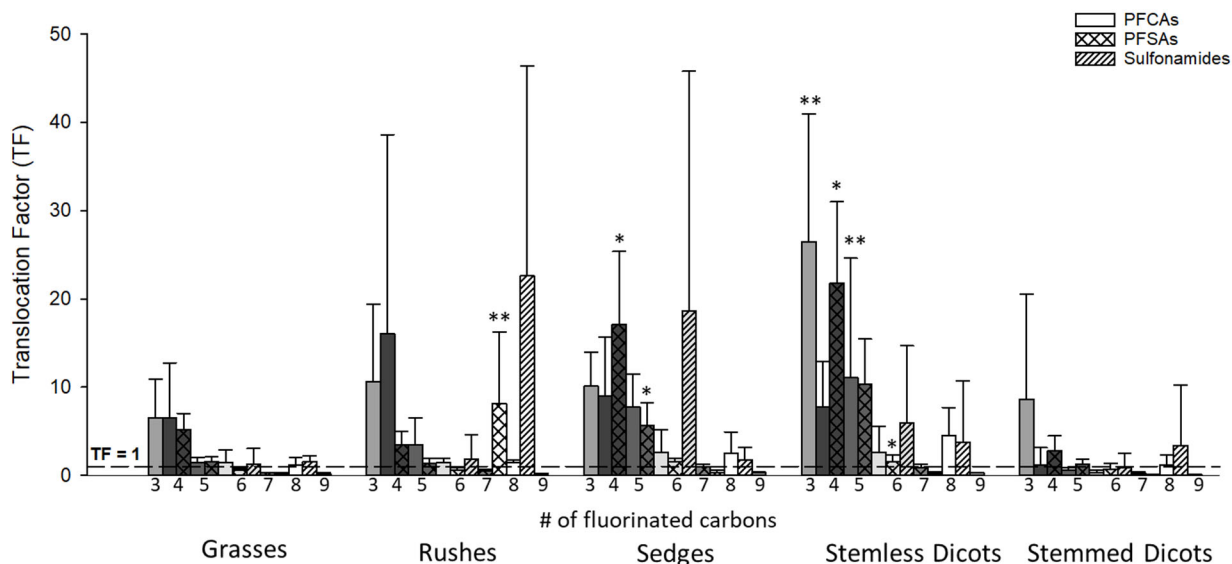


Figure 42: Translocation factors of all PFAS analyzed among plant groups. Error bars represent standard deviation.

“*” indicates TF is significantly greater than three other plant groups.

“***” indicates TF is significantly greater than all other plant groups.

Although grasses were some of the best PFAS accumulators, they were the second least efficient at translocation. However, nine out of thirteen PFAS had TF values greater than one in grasses, indicating that they were still efficient at transporting PFAS from root to leaves. Protein content is an important plant parameter for controlling translocation of PFAS, and was speculated to be important in explaining why sedges and stemless dicots were more efficient at translocating than other plant groups. To confirm this, additional work would need to analyze protein content of all plants studied, but that was outside the scope of this work.

Nutrient Results

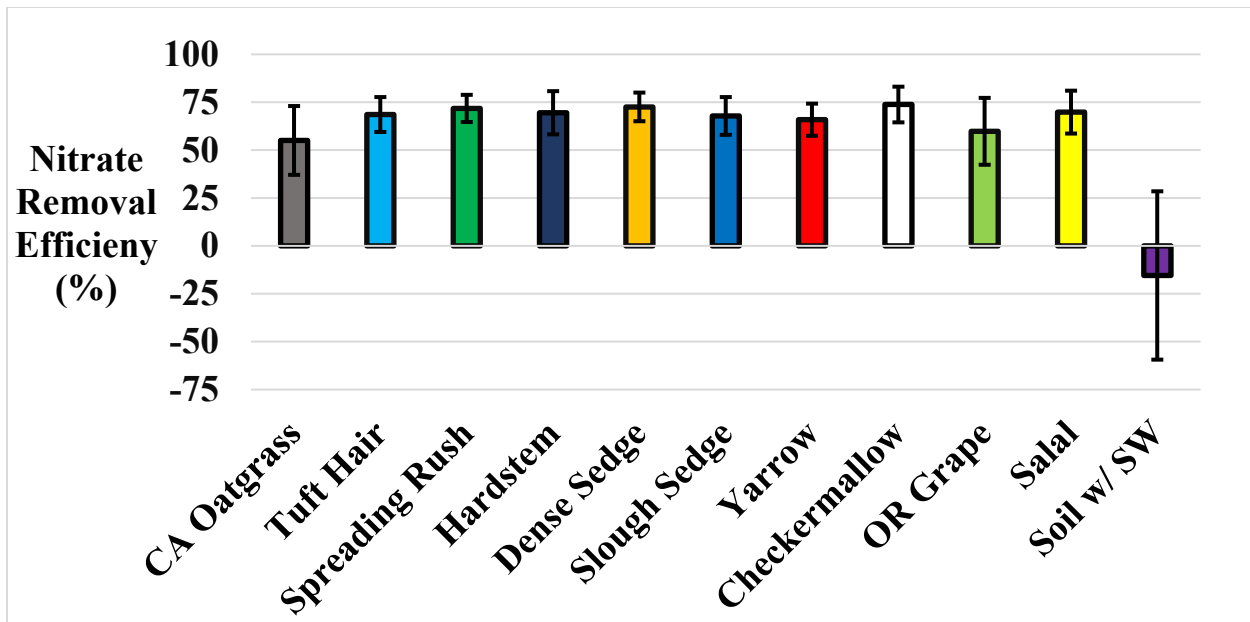


Figure 43: Nitrate Removal Efficiency by the different plant treatments. Error bars represent 95% confidence intervals.

All plants removal of nitrate was statistically indistinguishable from the removal performed by the other plants. However, all plants outperformed the soil-only control (“Soil w/ SW”).

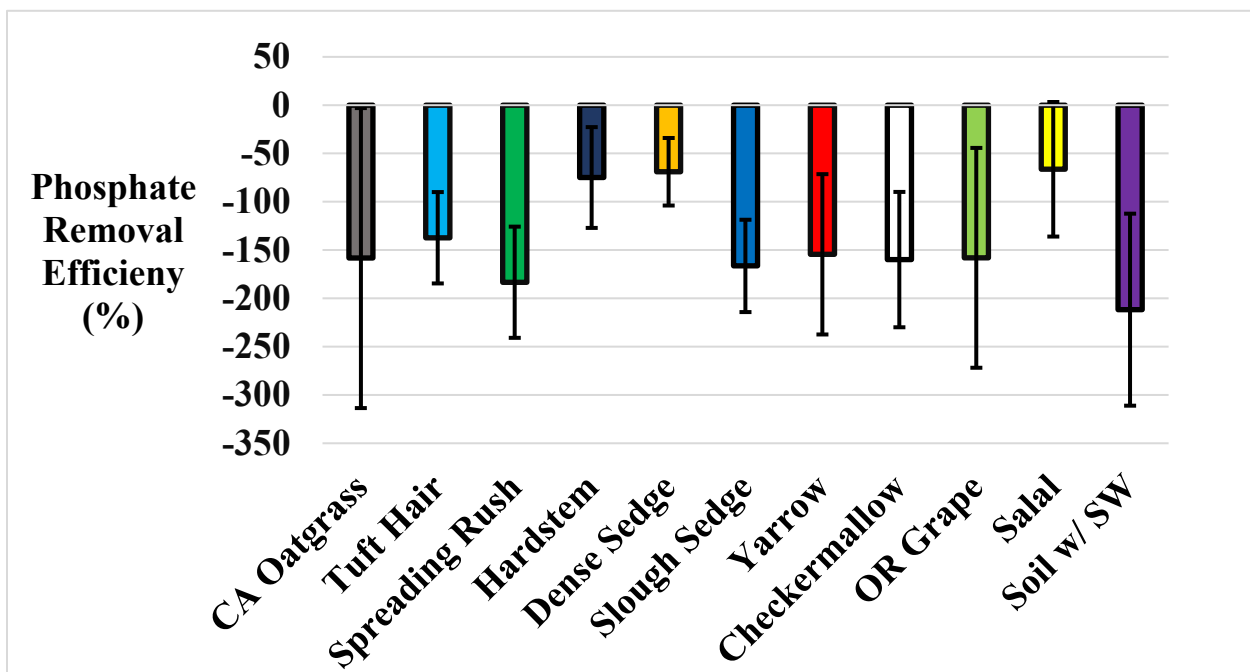


Figure 44: Phosphate Removal Efficiency by the different plant treatments. Error bars represent 95% confidence intervals.

Phosphate “removal” was far more variable across the different plant treatments, though all systems were net exporters of phosphate. Much as with dissolved copper, the compost used in these units (as in real systems) proved a significant source of phosphate. However, salal, hardstem bulrush, and dense sedge performed the best at limiting export of phosphate.

Task 3

For Task 3, field data was collected to characterize variability in system processes relevant to the treatment train, many of which were previously studied only under controlled laboratory and greenhouse conditions in Objectives 1-2. These included:

1. Characterization of transport of sediment-associated PFAS compounds in LID using sediment tracer studies.
2. Temporal characterization of plant stress in bioretention cell during wet and dry periods in the field.
3. Hydrologic performance of treatment train over multiple storms
4. Contaminant treatment performance of treatment train over multiple storms.

Below is a summary of the results obtained so far at the end of this project. We will continue to collect data in the newly constructed treatment train in the year 2022 after the end date of this current project as this data is crucial for completion of Tasks 4.1-4.2 that had been significantly influenced by COVID-19 related delays.

Sediment Tracer Study

In Tasks 3.1-3.2, a sediment tracer study was conducted to improve understanding of sediment transport at the OGSIR field site and the developed treatment train. This portion of the project therefore required baseline measurements of the pre-existing sediment conditions at OGSIR. Results of a particle size analysis are shown in Figure 45. The bulk soil at the field site is composed of approximately 50% fines ($<70\ \mu\text{m}$). The prevalence of fines led us to focus the tracer study primarily on surficial transport and deposition, since infiltration rates at the field site are generally slow: A constant head saturated hydraulic conductivity analysis of the OGSIR soil found $K_s = 6\ \text{m/d}$. Spatial and temporal variability of sediments was characterized by repeating the PSD analysis for each of the 3 GI cells at OGSIR, noting that at the time of sampling cell 1 had been previously undisturbed (covered and non-vegetated) while cells 2-3 had well-established vegetation and had been subject to multiple years of stormwater inflow.

Sediment samples were analyzed at three locations along each cell, and at different depths. The results, Figure 46, showed that the cells exposed to stormwater inflow had a relatively lower fraction of fine sediment. All three cells were initially installed with identical soil, hence the reduction in fines in cells 2-3 indicates active sediment transport is occurring causing fine sediment to be exported when the cells are exposed to stormwater flow. Lastly, to determine the contaminant effects of the fine sediment export, an analysis was conducted to quantify sediment-borne contaminant load on a per-size-fraction basis. The results showed contaminant load increased with decreasing particle size, as would be expected due to the larger surface area associated with smaller particles, with one exception of Fe which had greatest contaminant load for sizes $25\text{-}75\ \mu\text{m}$. This led us to specify a tracer particle size of $40\ \mu\text{m}$, which was also the

finest size the manufacturer was able to produce. The tracer particles have a narrow size distribution (Figure 45) and have a specific density similar to that of natural soil, 2650 kg/m³.

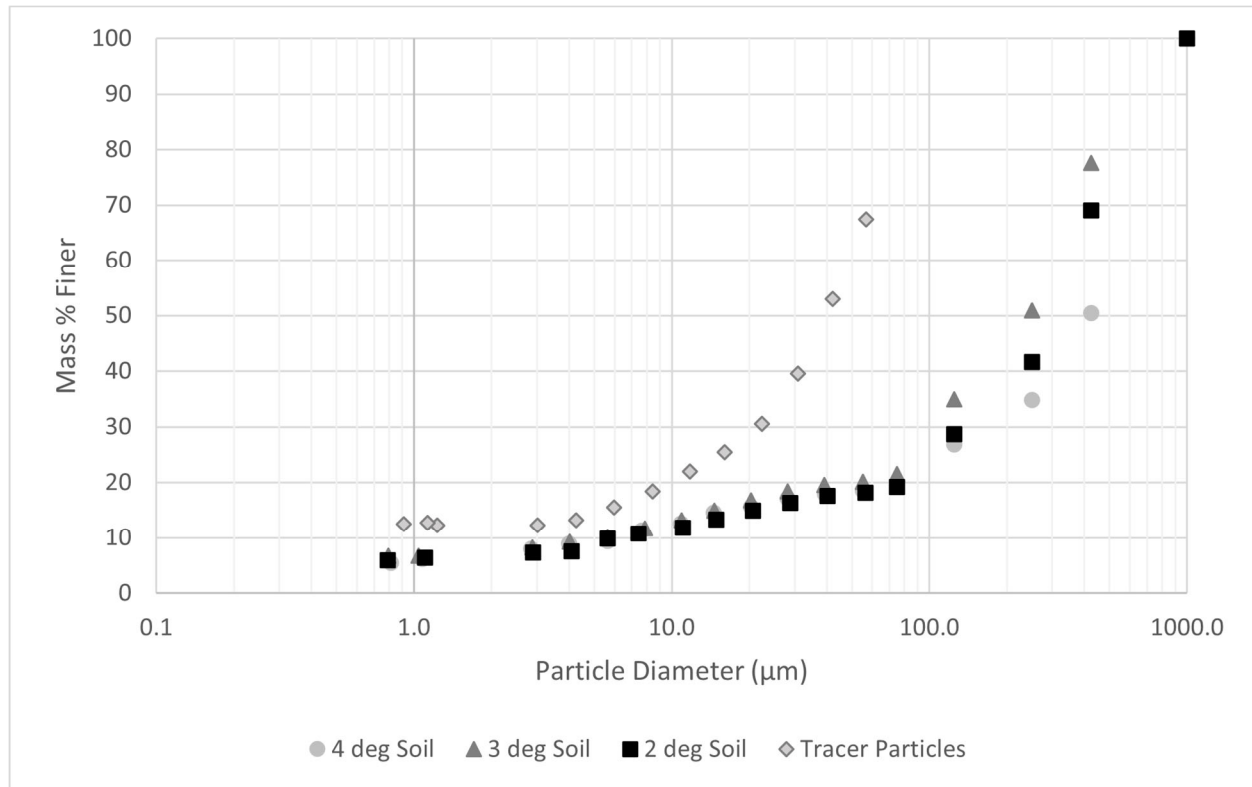


Figure 45: Particle size distribution of dual-signature tracer particles (diamonds), and OGSIR soil used in tracer experiments.

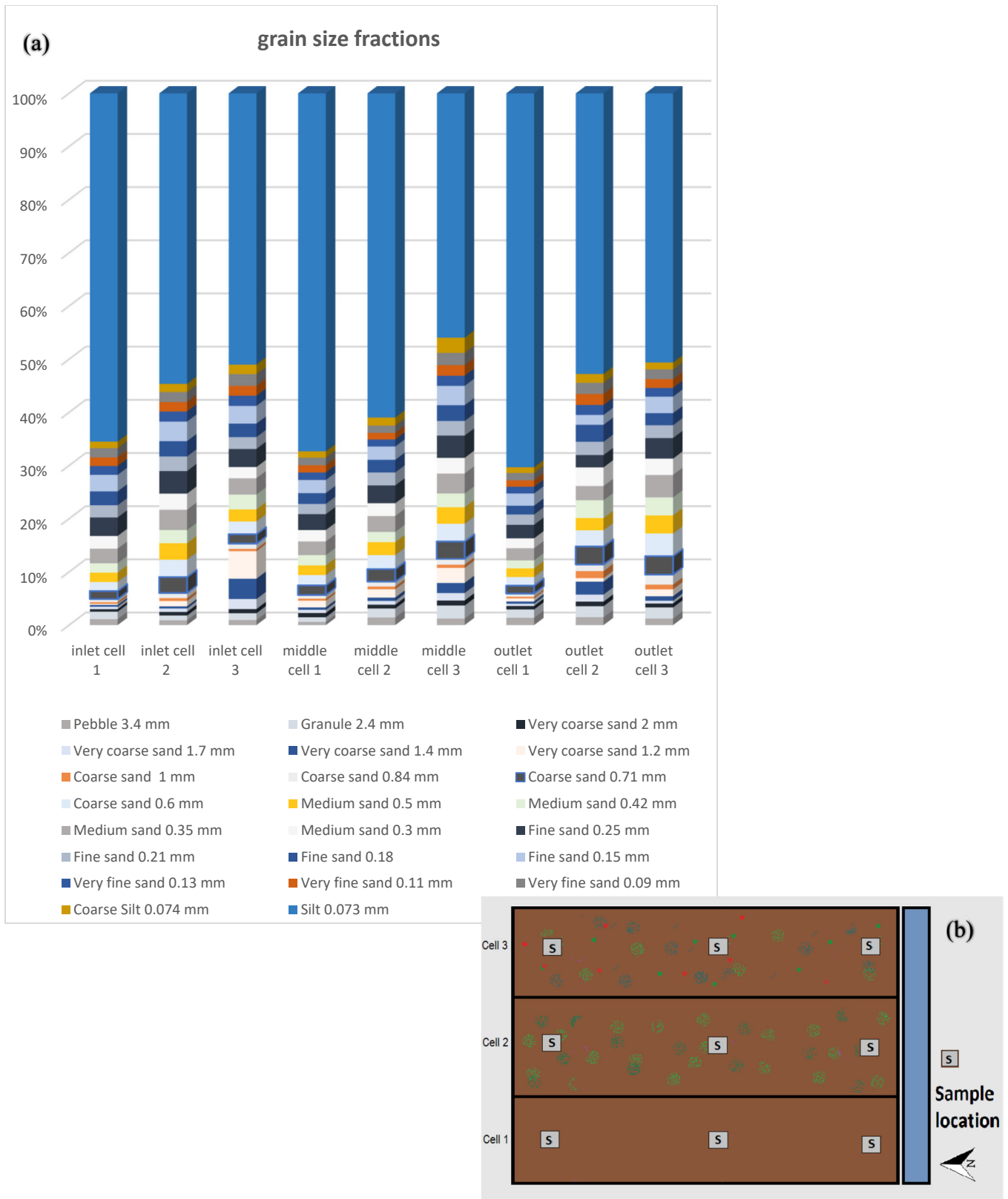


Figure 46: (a) Particle size distributions at the inlet, middle, and outlet of each of the 3 GI cells at the OGSIR field site; (b) sample locations shown in inset.

The overall aim of the tracer study was to determine the rate of transport of the fine sediment under the conditions present in the LID part of the developed treatment train. Our original intention was to conduct the tracer study on-site, once the treatment train had been installed. In the year 1 of the project we tested experimental methods for deploying and sampling tracers in-situ, in anticipation of a year 2-3 tracer study at OGSIR. However the timing of the treatment train installation and ability to do field work then became severely limited by COVID-19. Therefore, we chose to pursue the tracer study in the form of idealized flume experiments, with the goal of developing a theoretical sediment transport model that could be used in future analysis of the treatment train. To our knowledge, no sediment transport formula currently exists to predict the dynamic transport of fine sediments in stormwater flowing over and within a natural soil bed, as in GI treatment trains. The challenges in developing such a model stem from the fact the transport occurs in a very thin saturated layer of soil on the surface of the LID, whereas most sediment transport models assume transport is driven by shear stress in a fully-developed fluid boundary layer above a sediment bed. The sediment tracer methodology is, however, capable of measuring near-surface sediment transport in very shallow flow, without disturbing the bed, and hence was ideally suited for our study. A series of tracer flume experiments were performed that led to development of a new model for fine sediment transport in LID-like conditions. The new model extends an existing model commonly used for sediment transport over grass filter strips (Deletic, 2001); the extensions incorporate experimentally determined parameterizations relevant to the OGSIR field site, including a dependence of sediment deposition on bed slope that had not been observed previously. The new model also adds a representation of the “clogging” effect that occurs when high concentrations of fine sediment are present in the influent stormwater. More details on the theoretical and experimental results can be found in Wells (2021, MS Thesis), and Wells & Wilson (in-revision).

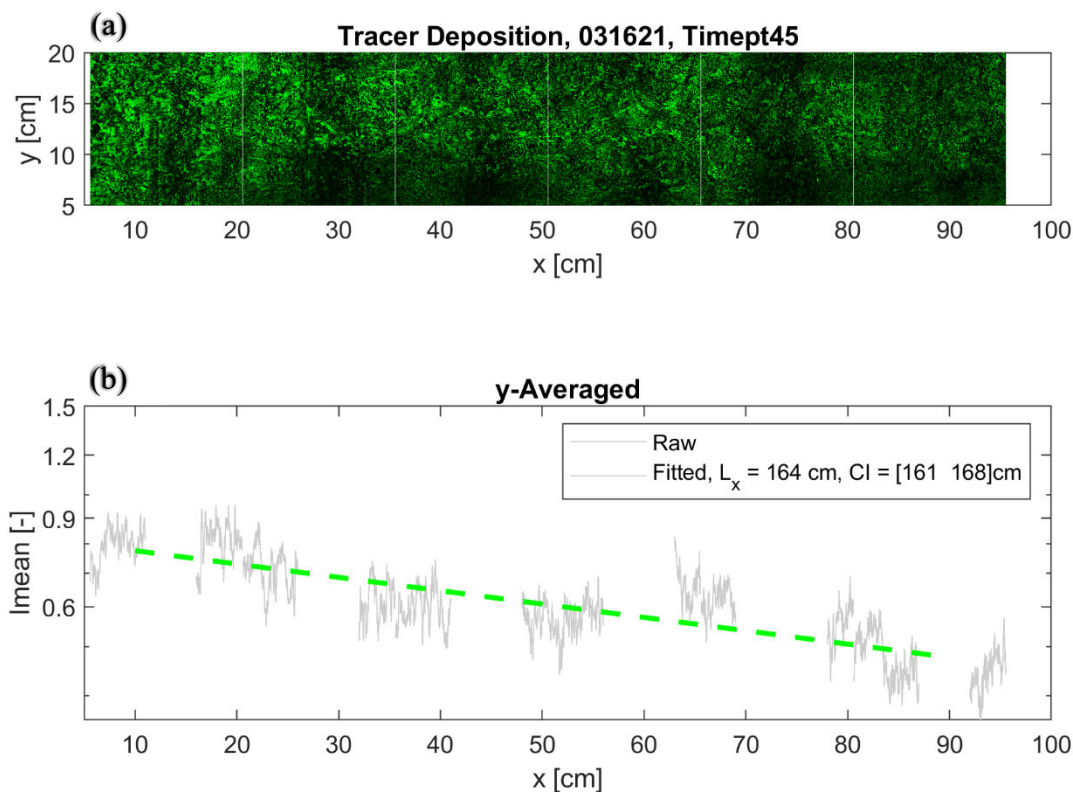


Figure 47: Example sediment tracer measurements in experimental flume. (a) Upper panel shows spatial distribution of tracer measured by camera hood (Figure 45). (b) Lower panel shows how the transverse-averaged tracer concentration was fitted to a model (Wells & Wilson, in-revision) to determine a deposition rate that in turn governs overall sediment transport.

Temporal characterization of plant stress

Uptake of contaminants by plants is an important process that influences treatment of stormwater in nature-based passive stormwater technologies. However, to support function and performance of plants in GI, vegetation health-monitoring practices must be established. Monitoring the health of vegetation in GI can reveal signs of water stress, pollutant induced toxicity, and disease, as well as provide insight into important parameters necessary to model plant biomass changes over time in stormwater models of LID-based treatment trains. In this study (Prettyman et al., 2021), the feasibility of using uninhabited aircraft systems (UAS), in comparison to standard ground-based methods (specifically, fraction of intercepted photosynthetically active radiation (fIPAR) using a ceptometer), was investigated as a methodology for monitoring biomass and primary production in bioswale cells at OGSIR facility (Figure 48–Figure 49). Implementation of the UAS-based approach involved flight planning in an urban area to meet resolution requirements of bioswale imagery obtained from near-infrared and red-green-blue cameras. The resulting normalized difference vegetation index (NDVI) estimated from UAS data was tracked over a 2-month period in 2019 at the existing bioswale cells 1, 2, and 3 during the

transition from wet spring to dry summer, showing the spatial distribution of NDVI and the change in vegetation coverage areas over time. For example, Figure 50 shows classified NDVI maps of the existing OGSIR bioswale facility for the three dates, where NDVI values are classified from -1.0 to 1.0. The shades of green represent healthy vegetation, yellow represents senescent or fading vegetation, orange and brown represent soil and dead vegetation, and red represents no vegetation. The values close to -1 are in the gravel/rock on the side of the rain garden. Cell 1 contains only weeds, showing the effect they have on the NDVI in all cells in the data sets. Once these weeds die, the remaining green areas in Cells 2 and 3 represent the original vegetation planted in the facility in 2014. The largest concentration of green values, or healthy vegetation on June 29 and July 27, was close to the inlet on the south end of the facility, with the coverage of green values decreasing at one-third of the length of the facility and continuing to decrease moving away from the inlet.

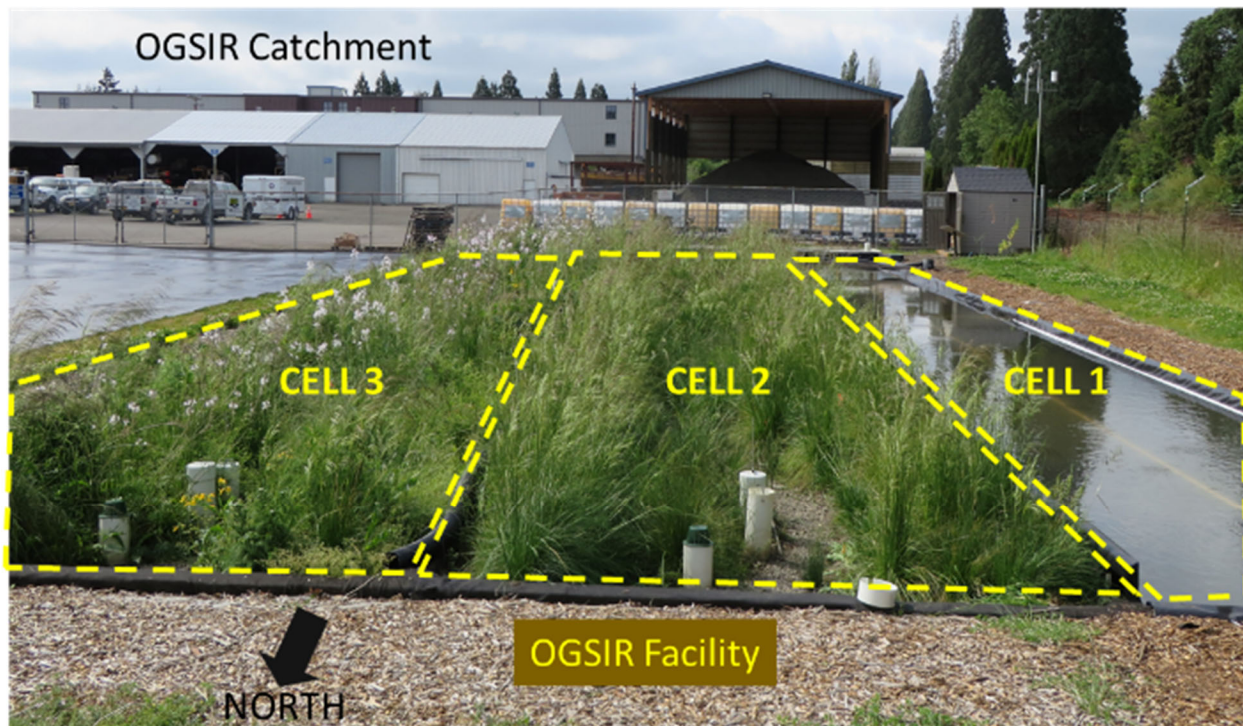


Figure 48: Cells in OSU-Benton County Green Stormwater Infrastructure Research (OGSIR) facility, and the catchment at far end.

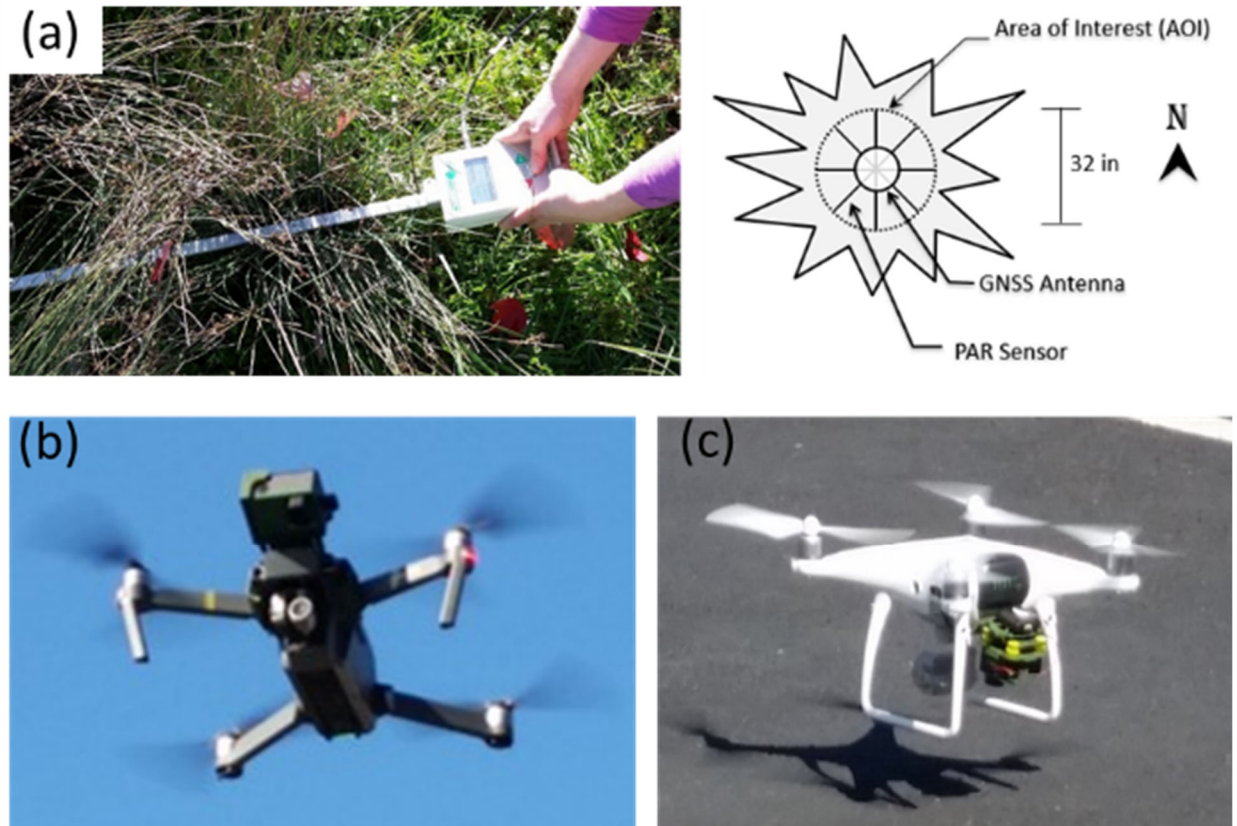


Figure 49: (a) Accupar LP-80 ceptometer for measuring fiPAR manually; DJI Mavic Pro, (b) and DJI Phantom 4 Pro, (c) both showing the externally mounted MAPIR Survey3N NIR camera.

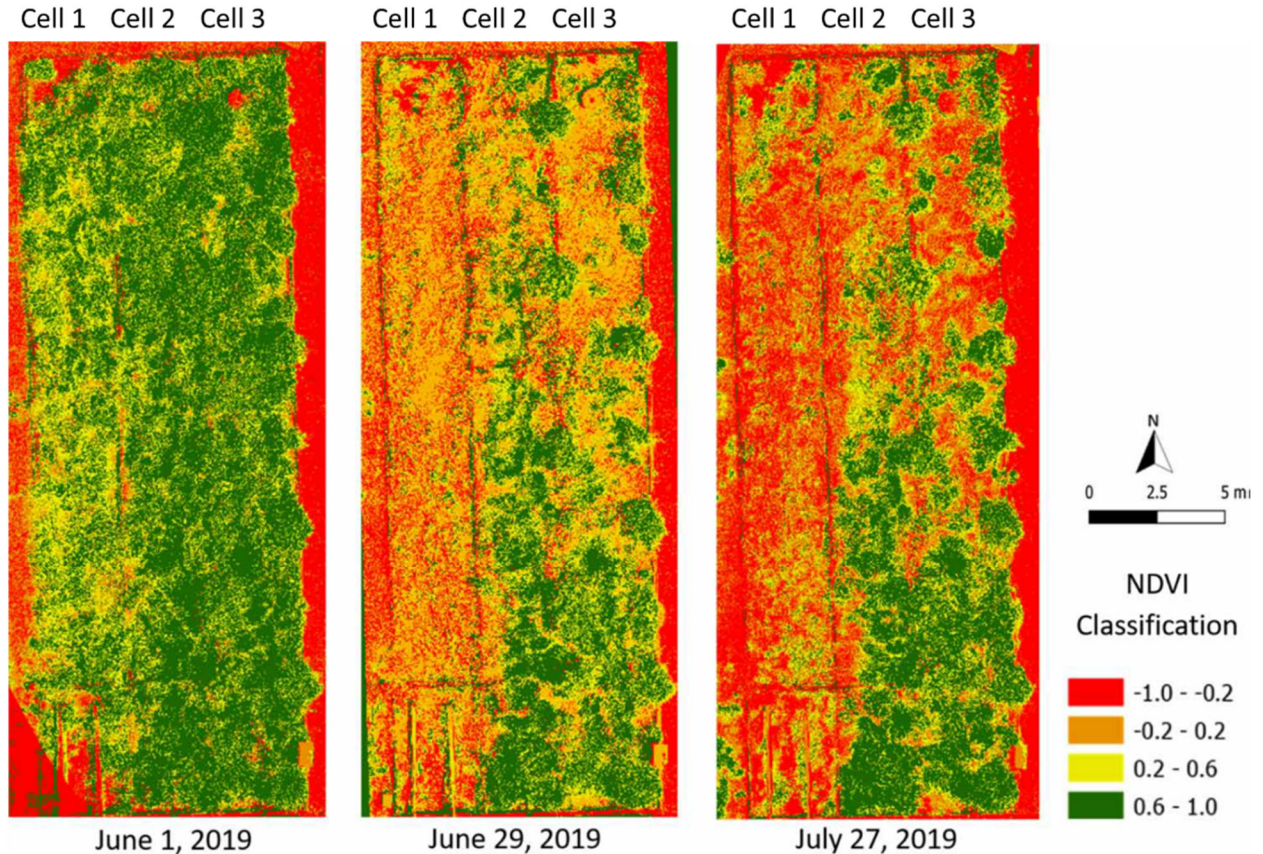


Figure 50: Classified NDVI data for the three dates showing the spatial distribution of NDVI values in three OGSIR cells

Figure 51 shows the scatter plots and regression models to determine the NDVI relationship to fIPAR for sedge (a), rush (b), and broad leaf (c) vegetation groups in the bioswale cells, using the data collected on June 29, 2019. It appears that the broad leaf and sedge NDVI-fIPAR relationship is stronger with coefficients of determination (R^2) of 0.64 and 0.55, with a very weak relationship for the rush group ($R^2 = 0.12$). Since the vegetation groups have small sample sizes, there is a potential for outliers to affect the regression model. For example, in Figure (c), the low point (bottom left of the figure) appears to have both high influence and leverage on the regression analysis. This outlier may be a function of the small sample size. Future studies are recommended to take this issue into consideration when collecting additional fIPAR samples of each vegetation group, so that the relationship for different types of stormwater GI vegetation species can be determined more accurately.

Overall, ground-based measurements of the fraction of intercepted photosynthetically active radiation (PAR) presented multiple practical challenges during implementation in the field, leading to over- and underestimates of intercepted PAR. Finally, UAS-derived NDVI was found to be a valuable reflectance-based, vegetation health-monitoring methodology that can be used by utilities and cities for practical, cost-effective, and rapid assessment of vegetation stress,

monitoring plant growth and senescence, and for long-term maintenance in green stormwater facilities.

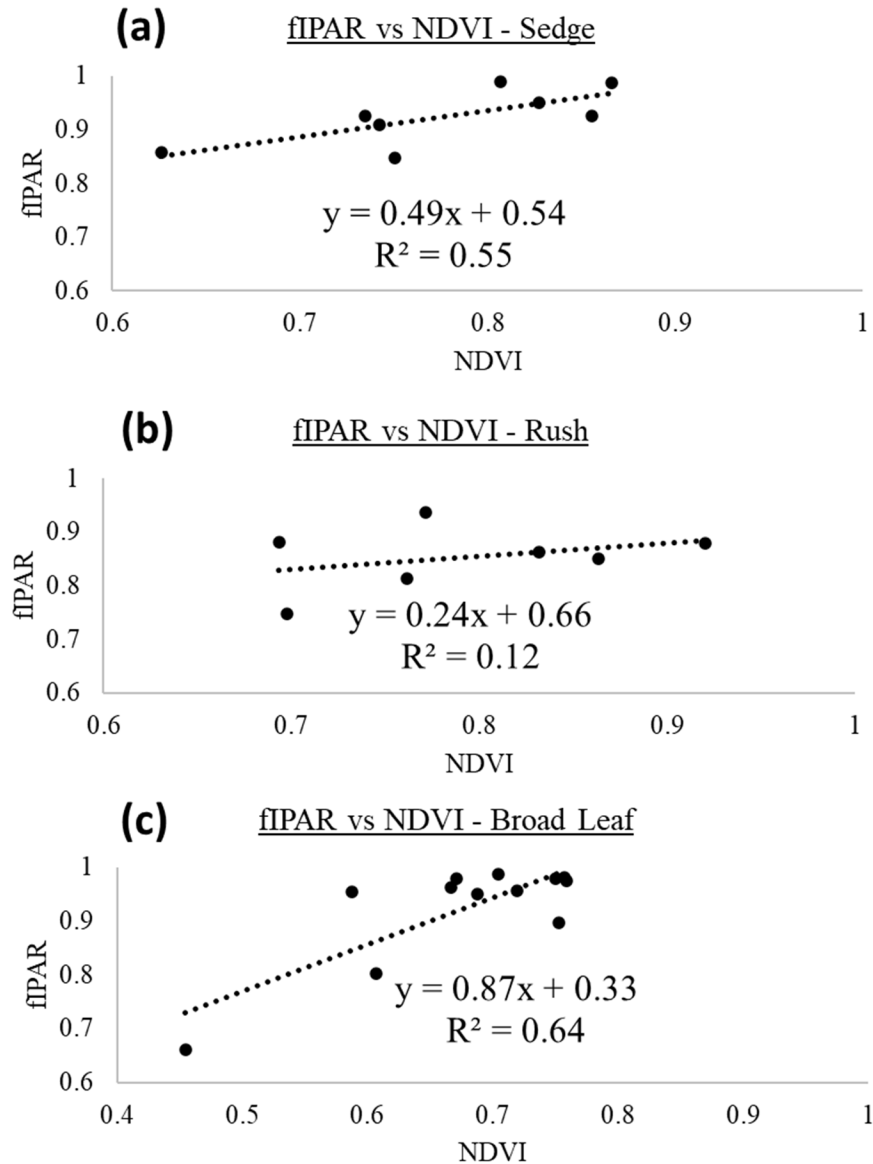


Figure 51: Scatter plots and regression models of the NDVI relationship to fIPAR of sedge, rush, and broad leaf vegetation groups including vegetation from both cells of the OGSIR facility for data collected on June 29–30, 2019.

Hydrologic and contaminant treatment

The treatment train performance analysis focuses on commonly monitored water quality analytes including solids, metals, and nutrients, as summarized in

Table 7 below.

Table 7: Analyzed Constituents by Category.

Solids	Total suspended solids (TSS)
	Total dissolved solids (TDS)
Conventional	pH
	Temperature
	Electric conductivity (EC)
	Total hardness
	Total alkalinity
Nutrients	Total phosphorus
	Orthophosphate
	Total nitrogen
	Total Kjeldahl nitrogen (TKN)
	Nitrate + Nitrite (NO _x)
Metals (totals and dissolved)	Copper
	Zinc
Hydrocarbons	Polycyclic aromatic hydrocarbons (PAHs)

A total of six storms were sampled using ISCO samplers, over the period of 8 months representing different storm durations, sampling intervals, and periods of storms sampled by four ISCOs at different junctions of the treatment train, as described in

Table 8. Table 9 summarizes the hydrological and site conditions for all monitored storms. Since the inflow into the LID is obtained from a pump at the OGSIR facility via Junction 0 and spread over the LID surface via perforated drain hose (Figure 4–Figure 6), values for incoming pumped discharge rate (cfs) per LID area (sq. ft) were calculated at an hourly scale to estimate an equivalent hourly specific discharge in in/hr entering LID every hour (Equation 3). Storm 1 experienced a total of 7.10 inches specific discharge over the duration of the storm (Column 2 in

Table 8), with an average hourly specific discharge of 0.51 in/hr. Storm 2 had a slightly higher value of total specific discharge at 8.13 in, and with an average 0.34 in/hr hourly specific discharge. Storm 3 had a smaller value of total specific discharge at 3.43 in, with 0.45 in/hr hourly specific discharge. Storm 4 experienced a total of 7.0 inches specific discharge with an average of 0.58 in/hr specific discharge, which was similar to the intensity of storm 1. Storm 5 had a total of 4.70 inches specific discharge with an average hourly specific discharge of 0.39 in/hr. Storm 6 had the highest values of total specific discharge of 10.5 inches with an average hourly specific discharge of 0.65 in/hr (Table 9).

$$I = \frac{\text{Flow over thermal weir, cfs}}{\text{LID area, ft}^2} \left(\frac{12 \text{ inches}}{1 \text{ ft}} \right) \left(\frac{3600 \text{ seconds}}{1 \text{ hr}} \right)$$

(Equation 3)

Where the LID area is the surface area of 27 ft x 10.8 ft.

Table 8: Storm Sampling Summary.

Storm ID	Overall Storm Duration	ISCO Sampling Frequency	Location and Period of Storm Sampled			
			Junction 0 (LID Inlet)	Junction 1 (LID Outlet)	Junction 3 (after Biochar)	Junction 4 (after Rembind)
1	12-hr storm [6 PM- 6 AM (+1 day)]	30-min interval	6:00 PM – 5:30 AM (+1 day)	7:00 PM – 6:30 AM (+1 day)	7:00 PM – 6:30 AM (+1 day)	9:00 PM – 9:30 AM (+1 day)
2	24-hr storm [2 PM – 1 PM (+1 day)]	1-hr interval	2:00 PM – 1:00 PM (+1 day)	3:00 PM – 2:00 PM (+1 day)	3:00 PM – 2:00 PM (+1 day)	4:00 PM – 3:00 PM (+1 day)
3	<12-hr storm (2 PM – 10 PM)	20-min interval	2:00 PM – 9:40 PM	5 AM – 9 AM; 2 PM*	3:00 PM – 10:40 PM	3:00 PM – 10:40 PM
4	<12-hr storm [6 PM – 2 AM (+1 day)]	20-min interval	6:00 PM – 1:40 AM (+1 day)	7:30 PM – 3:10 AM (+1 day)*	7:30 PM – 3:10 AM (+1 day)	7:30 PM – 3:10 AM (+1 day)
5	12-hr storm (4 AM – 4 PM)	30-min interval	4:00 AM – 3:30 PM	4:00 AM – 3:30 PM ^a	4:00 AM – 3:30 PM	4:00 AM – 3:30 PM
6	24-hr storm [5 PM – 4 PM (+1 day)]	1-hr interval	5:00 PM – 4:00 PM (+1 day)	5:30 PM – 4:30 PM (+1 day)	5:30 PM – 4:30 PM (+1 day)	5:30 PM – 4:30 PM (+1 day)

Note: * limited number of samples was collected due to technical problems with ISCO sampler.

Table 9: Hydrological Monitoring Data Summary.

Storm ID	Event Date	Preceding # of Dry Days	Peak Flow, gpm	Average Pump Flow Intensity per LID Area, in/hr	% Overlap between Pumping Duration and ISCO Sampling Duration at LID Inlet	Total Pumped Flow Volume Entering LID, gallons
1	10/12/2021	1	3.59	0.51	81.6	1262
2	10/25/2021	0	2.67	0.34	96.8	1450
3	11/12/2021	0	2.50	0.45	73.5	611
4	01/30/2022	3+	2.63	0.58	99.6	400
5	03/21/2022	0	2.43	0.39	100	836
6	04/10/2022	0	2.74	0.65	96.8	2160

Table 10 reports the minimum detection limits for analyzed water quality parameters that were restricted by the analysis methods (i.e., TNT kits range). The sample was diluted with DI water where constituent values exceeded detection maximum limit. Field and laboratory blanks were used to calibrate measured concentrations of collected samples, in order to account for the baseline contamination in equipment used in the field and laboratory. The following (Equation 4 and (Equation 5 illustrate how the concentrations of Field Blank (A) and Lab Blank (B) were used to calibrate the sample concentration (X) analyzed for a water quality parameter.

$$\text{Corrected Field Blank } A' = \text{Original Field Blank } A - \text{Lab Blank } B$$

(Equation 4)

$$\text{Corrected Sample } X' = \text{Original Sample } X - \text{Corrected Field Blank } A'$$

(Equation 5)

Table 10: Minimum Detection Limit for Analyzed Constituents.

Parameter	Method Used	Detection Minimum Limit	Detection Maximum Limit
Alkalinity, total	Hach 10239 (Colorimetric)	25 mg/L CaCO ₃	400 mg/L CaCO ₃
Hardness, total	SM 2340 B	1 mg/L CaCO ₃	20 mg/L CaCO ₃
Total Nitrogen	Hach 10208 (Persulfate Digestion)	1 mg/L N	16 mg/L N
Nitrite	EPA 354.1; SM 4500-NO ₂ B	0.015 mg/L NO ₂ -N	0.6 mg/L NO ₂ -N
Nitrate	40 CFR 141/136	0.23 mg/L NO ₃ -N	13.5 mg/L NO ₃ -N
Total Phosphorus	EPA 365.1	0.15 mg/L PO ₄	4.5 mg/L PO ₄
Orthophosphate	EPA 365.3	0.15 mg/L PO ₄	4.5 mg/L PO ₄
COD	Hach Method 8000; 40 CFR 136.3	3 mg/L COD	150 mg/L COD
Copper (dissolved and total)	Standard method 3125; Samples prepared as per standard method 3030D	0.003215 ppb	—
Zinc (dissolved and total)	Standard method 3125; Sampled prepared as per standard method 3030D	0.053623 ppb	—
Polyaromatic Hydrocarbons (PAHs)	Extraction method based on Aqeel et al., 2010 and EPA 550.1; GC/MS method based on Trine et al., 2019; details below	See Error! Reference source not found. for details; $\approx 0.11 \text{ pg/mL} = 1.1 \cdot 10^{-3} \text{ ug/L}$	—

Turbidity/Flow

Figure 52–Figure 54 show the turbidity time series for 3 of the 6 monitored storms.

Table 11 summarizes turbidity data for all monitored events.

For storm 1, turbidity ranges from 17.8 – 159.5 NTU (nephelometric units) with an average of 78.2 ± 44.2 NTU at inlet, 3.75 – 38.0 NTU with average of 23.19 ± 10.5 NTU at LID outlet, 2.17 – 7.75 NTU with an average of 5.21 ± 1.93 NTU after biochar, 7.49 – 18.9 NTU with an average 15.25 ± 3.82 NTU at treatment train outlet.

For storm 2, turbidity ranges from 18.8 – 375.6 NTU with an average of 119.7 ± 108 NTU at inlet, 10.7 – 60.3 NTU with average of 33.5 ± 15.9 NTU at LID outlet, 10 – 17.3 NTU with 14.6 ± 1.79 , and 16 – 31.7 NTU with 25.5 ± 3.99 NTU between treatments (after biochar) and at train outlet, respectively.

For storm 3, turbidity ranges from 1.41 – 86 NTU with an average of 53 ± 19.4 at inlet, 8.61 – 21.4 NTU with 13.4 ± 4.70 NTU at LID outlet, 4.97 – 8.05 with average of 6.77 ± 1.08 NTU between treatments, and 12.1 – 16.3 NTU with an average of 14.2 ± 1.30 NTU at train outlet.

For storm 4, turbidity ranges from 51.7 – 308 NTU with an average of 229 ± 44.2 NTU at inlet, 7.06 – 51.2 NTU with average of 13.3 ± 10.5 NTU at LID outlet, 4.13 – 6.21 NTU with an average of 5.11 ± 1.93 NTU after biochar, 8.03 – 8.75 NTU with an average 8.31 ± 0.20 NTU at treatment train outlet.

For storm 5, turbidity ranges from 11.6 – 162 NTU with an average of 34.7 ± 108 NTU at inlet, 3.79 – 37.7 NTU with average of 5.95 ± 2.7 NTU at LID outlet, 3.60 – 5.48 NTU with 4.42 ± 1.79 , and 10.1 – 15.6 NTU with 12.2 ± 3.99 NTU between treatments (after biochar) and at train outlet, respectively.

For storm 6, turbidity ranges from 17.6 – 192 NTU with an average of 51.6 ± 19.4 at inlet, 1.85 – 31.8 NTU with 2.63 ± 0.80 NTU at LID outlet, 2.97 – 4.11 with average of 3.21 ± 1.08 NTU between treatments, and 5.26 – 9.46 NTU with an average of 6.86 ± 1.30 NTU at train outlet.

The monitored storms show consistent trend of higher turbidity at the inlet with maximum value of 376 NTU during storm 2. The LID cell in the treatment train indicates the highest reduction in turbidity, as seen by the reduction in turbidity peaks from LID inlet (Junction 0) to LID outlet (Junction 1), which are much higher than the reduction obtained from Biochar and Rembind cells. The low values of turbidity entering the LID inlet (max of 86 NTU) during the third monitored storm (in comparison to Storms 1 and 2) can be explained by continuous rainfall preceding the monitoring event.

Table 11: Turbidity Data Summary.

I D	Location											
	LID Inlet			LID Outlet			After Biochar			After RemBind		
	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean
1	17.8	159	78.2	3.75	38.0	23.2	2.17	7.75	5.21	7.49	18.9	15.3
2	18.8	376	120	10.7	60.3	33.5	10.0	17.3	14.6	16.0	31.7	25.5
3	1.41	86.0	53.0	8.61	21.4	13.4	4.97	8.05	6.77	12.1	16.3	14.2
4	51.7	308	229	7.06	51.2	13.3	4.13	6.21	5.11	8.03	8.75	8.31
5	11.6	162.2	34.7	3.79	37.7	5.95	3.60	5.48	4.42	10.1	15.6	12.2
6	17.6	192.2	51.6	1.85	31.8	2.63	2.97	4.11	3.21	5.26	9.46	6.86

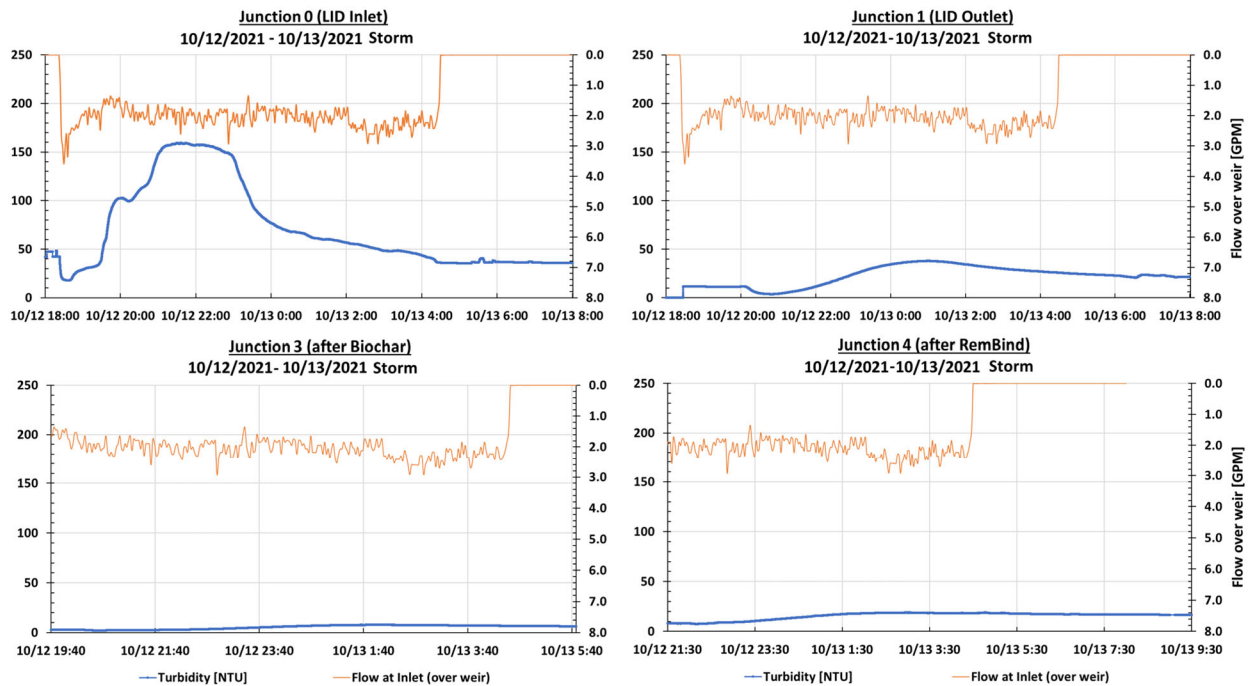


Figure 52: Turbidity time series of stormwater in Junction 0 (LID inlet), Junction 1 (LID outlet), Junction 3 (after Biochar), and Junction 4 (after Rembind) for storm on 10/12/2021–10/13/2021.

Secondary Y axis reports the flows in the LID inlet at the time turbidity data was logged.

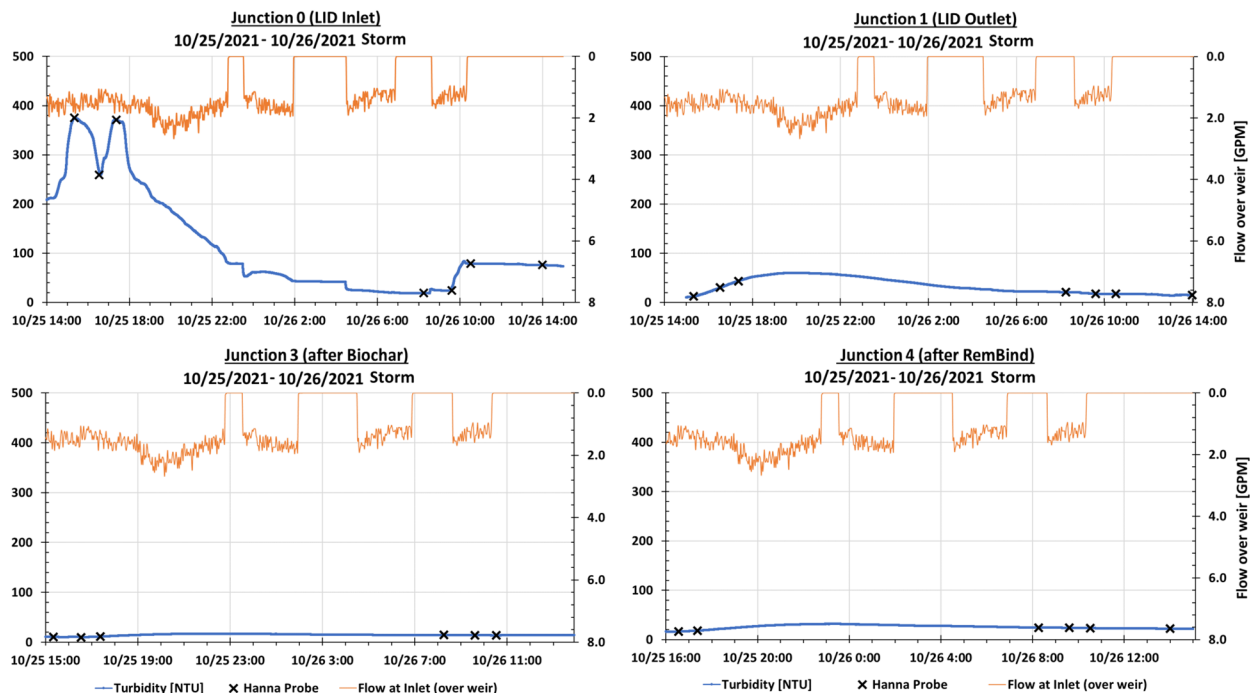


Figure 53: Turbidity time series of stormwater in Junction 0 (LID inlet), Junction 1 (LID outlet), Junction 3 (after Biochar), and Junction 4 (after Rembind) for storm on 10/25/2021–10/26/2021.

Secondary Y axis reports the flows in the LID inlet at the time turbidity data was logged. The cross marks indicate events when Hanna probe was used to manually measure pH, total dissolved solids (TDS), electrical conductivity (EC), and temperature.

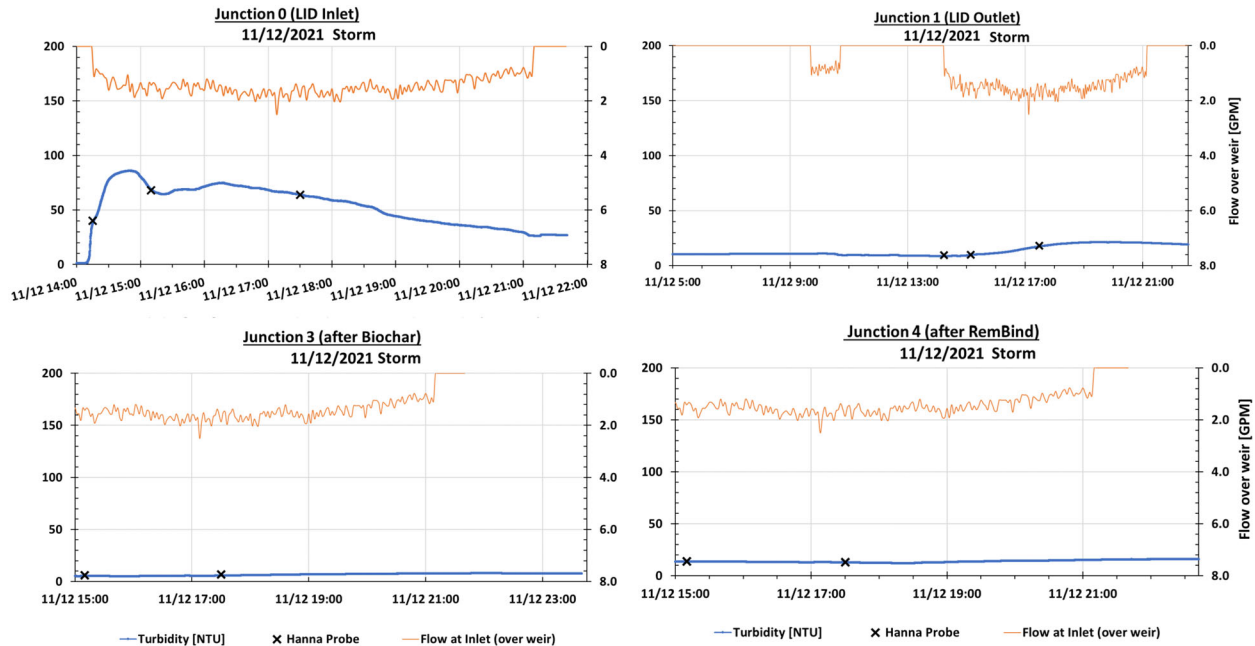


Figure 54: Turbidity time series of stormwater in Junction 0 (LID inlet), Junction 1 (LID outlet), Junction 3 (after Biochar), and Junction 4 (after Rembind) for storm on 11/12/2021.

Secondary Y axis reports the flows in the LID inlet at the time turbidity data was logged. The cross marks indicate events when Hanna probe was used to manually measure pH, total dissolved solids (TDS), electrical conductivity (EC), and temperature.

Overall, the treatment train system reduced turbidity from an average of 94 NTU at the influent to an average of 14 NTU at the effluent in the six monitored storms. A tendency of a slight increase in turbidity was, however, observed after Rembind treatment train for all six storms, as also illustrated in Figure 55 for three of the storms. The turbidity values are almost twice greater at treatment outlet after the Rembind treatment in comparison with the turbidity levels after Biochar treatment. This could be attributed to leaching fines, as also observed and shown in Figure 10. However, monitoring is currently continuing to evaluate when such behavior of fines leaching from the sorbent bins can be expected to terminate.

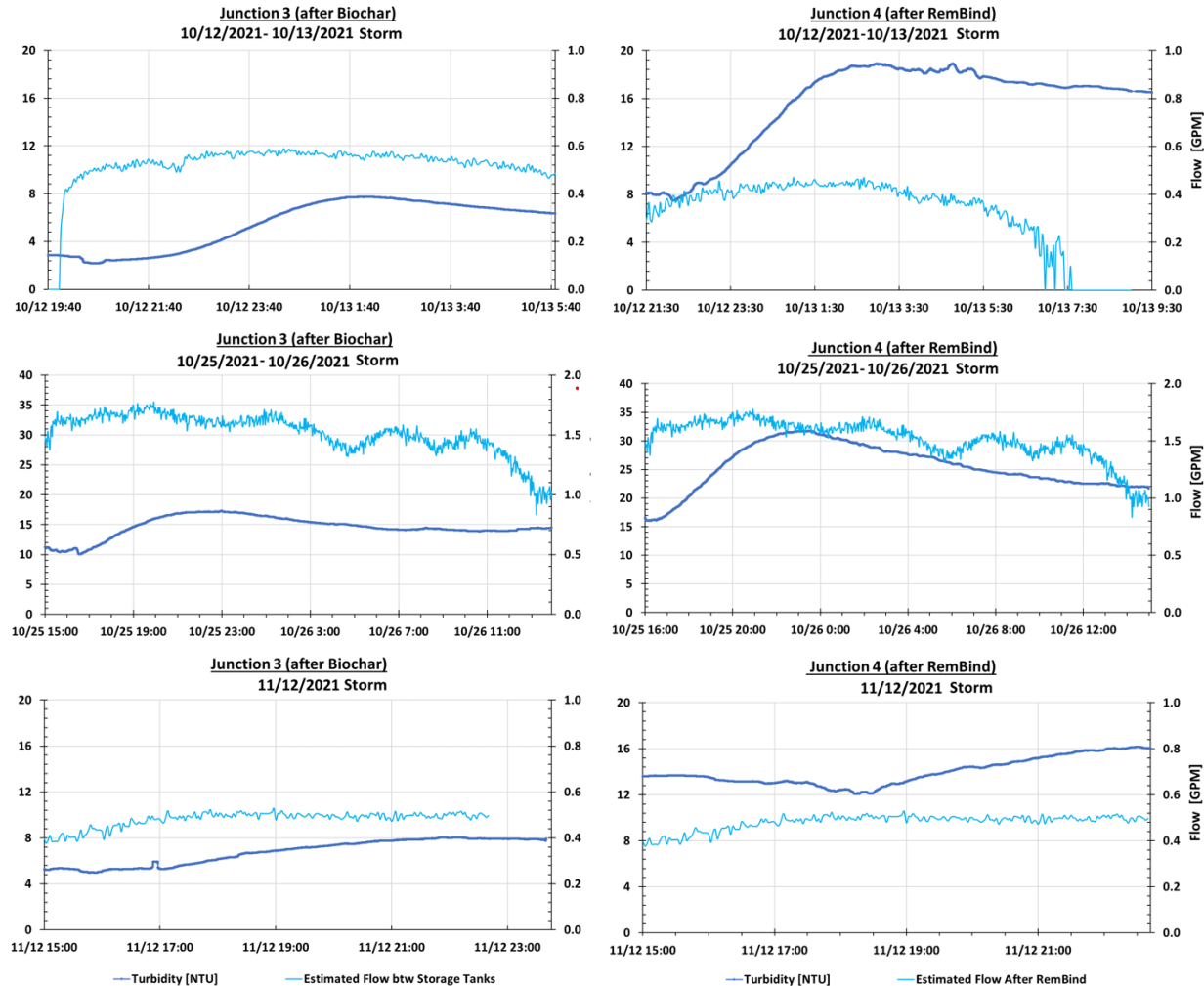


Figure 55: Turbidity behavior after Biochar (left graphs) and after Rembind (right graphs).

Residence Time

For storm 1 on October 12, 2021, turbidity data was analyzed to assess residence time of stormwater in the treatment train. Shifts in the turbidity values were manually identified to assess approximate residence time in the different sections of the treatment train.

For storm 1, the residence time between LID inlet and LID outlet was found to be approximately 1 hour 36 minutes, residence time between LID outlet and Junction 3 after biochar cell was found to be 21 minutes, and from Junction 3 via RemBind cell to Junction 4 was found to be 32 minutes. The total residence time for the entire treatment train was found to be close to 2 hours 29 minutes. The storms 2, 3, 5, and 6 monitored a single rain event within continuous storm, which made it more challenging to estimate residence time for the whole treatment train as the excess flows from previous single rainfall event were flowing through the system. Therefore, the residence time was found only for the bioretention cell. For storm 2, 3, and 6 the residence time

of only LID bioretention cell was found as 43 minutes, 29 minutes, and 25 minutes, respectively. In the events of storm 3 and 6, the bioretention was ponded and at least 6 inches of water above the soil was observed. For storm 4, the residence time was estimated to 1 hour 27 minutes. In the future, the construction of complete hydrograph of each treatment stage will be essential to understand the peak discharge reduction for the whole treatment train and the individual treatments. Moreover, it will help to understand how much of the pollutants observed within the monitored storm was contributed from the excess flow from previous event.

Storms 1 and 4 were the only storms among six monitored storms that had at least one preceding dry day at the time of sampling event. Therefore, the residence time of the treatment train can be assessed and compared with the results of storm 1. For storm 4, the residence time of LID cell was found to be approximately 1 hour 32 minutes, residence time between LID outlet and biochar cell was found to be 37 minutes, and between biochar and RemBind cells was found to be 10 minutes. The total residence time for the entire treatment train was estimated to be 2 hours 29 minutes, which agrees with the residence time of the treatment train during the storm 1.

It must be noted that the residence time of storms 3 and 6 monitored on November 12, 2021, and April 10, 2022, respectively, was assessed based on the first detected storm within 12 hours from start of the sampling. There was a difficulty of estimating residence time with pressure sensors for storm 3 and 6 due to the flow at LID outlet being accumulated from the previous storm. It also must be noted that the zero number of preceding dry days remained when used that approach meaning the light rain was observed within 12 hours at the site.

As more storms were monitored, the relationship between residence time and various storm characteristics, such as outflow to inflow relationship, pumped flow intensity, and number of dry days, were evaluated to understand unique bioretention characteristics that affect hydrologic performance of the treatment train. The only suggestive relationship ($R^2 = 0.77$) found in this evaluation was the ability of number of preceding dry days to be able to explain the variability of residence time in the bioretention cell. The residence time was estimated to be about 90 minutes when the soil in bioretention cell when there were one or more than one dry days before the storm. However, this time varied for wet soil conditions. Further Spearman's rank correlation test was performed to evaluate potential association between residence time and number of antecedent dry days. The analyses concluded no significant correlation to number of dry days. However, a larger sample of at least ten data points was required to consider this conclusion significant.

Solids

Total suspended solids (TSS) and total dissolved solids (TDS) were analyzed for storm composites from the samples collected using ISCO samplers at the four junctions. Figure 5 and Table 6 provides a visual and statistical summary of event mean concentrations (EMC) of TSS and TDS, at multiple junctions of the treatment train. Table 7 reports the percent reductions in EMCs of TDS and TSS for the entire treatment train, as well as reductions obtained at multiple stages of the train (i.e., LID inlet to LID outlet, LID outlet to outlet of Biochar cell, outlet of Biochar cell to outlet of Rembind cell). The treatment train system generally performed well with respect to TSS in terms of removal efficiency, with overall percent reductions of the treatment train being above 90% for all six storms. However, the train system showed an increase in TDS exported, as illustrated by negative reductions in EMCs in Table 7 for the overall treatment train. Specifically, the bioretention cell contributed to the largest increase in TDS concentrations with respect to EMC at the LID inlet. This can be ascertained from the increase

in average of EMC triplicates (Table 6) from 68 mg/L at LID inlet to 113 mg/L at LID outlet, leading to a significant increase by 66% relative to the EMC of 68 mg/L at the inlet. Treatment by Biochar led to a slight increase (17%) in values of triplicate average for before-treatment average EMC (113 mg/L) and after-treatment average EMC (132 mg/L), across the six storms. Treatment by Rembind led to a slight reduction (5%) in average EMC triplicates across six storms, with the triplicate average changing from 132 mg/L before treatment to 126 mg/L after treatment.

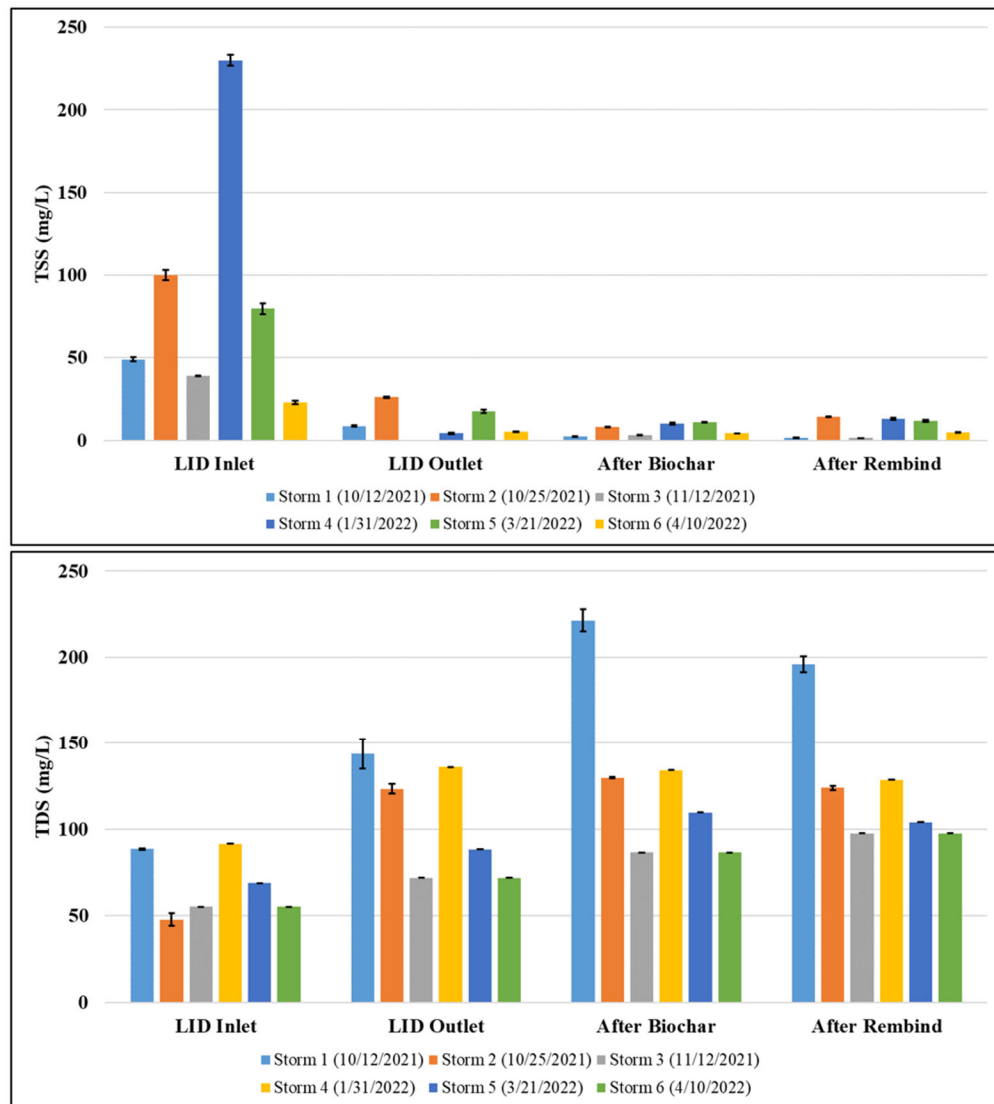


Figure 56: Summary of stormwater TSS and TDS EMCs. Error bar represents the variability between composite triplicates.

Table 12: Statistical summary of composite triplicates with respect to EMCs of TSS and TDS.

	Storm ID (Date)	LID Inlet	LID Outlet^a	After Biochar	After RemBind
TSS (mg/l)	Storm 1 (10/12/2021)	49.0 ± 1.20	8.70 ± 0.28	2.50 ± 0.08	1.70 ± 0.03
	Storm 2 (10/25/2021)	100 ± 3.12	26.1 ± 0.51	8.22 ± 0.19	14.2 ± 0.19
	Storm 3 (11/12/2021)	39.2 ± 0.19	- [*]	3.20 ± 0.08	1.30 ± 0.00
	Storm 4 (01/31/2022)	230 ± 3.33	4.29 ^a ± 0.40	10.3 ± 0.58	13.0 ± 0.58
	Storm 5 (03/22/2022)	79.7 ± 3.21	17.7 ± 1.00	11.1 ± 0.19	11.7 ± 0.58
	Storm 6(04/10/2022)	22.9 ± 1.07	5.20 ± 0.19	4.30 ± 0.00	4.80 ± 0.19
	Mean ± Std. Dev.	86.8 ± 75.5	12.4 ± 9.3	6.60 ± 3.73	7.80 ± 5.86
TDS (mg/L)	Storm 1 (10/12/2021)	88.4 ± 0.52	144 ± 8.71	221 ± 6.40	196 ± 4.70
	Storm 2 (10/25/2021)	47.7 ± 3.58	123 ± 2.86	130 ± 0.43	124 ± 1.13
	Storm 3 (11/12/2021)	56.5 ± 3.57	- [*]	109 ± 2.20	108 ± 1.84
	Storm 4 (01/31/2022)	91.5 ± 0.00	136 ^a ± 0.00	134 ± 0.00	129 ± 0.00
	Storm 5 (03/22/2022)	68.8 ± 0.00	88.2 ± 0.00	110 ± 0.00	104 ± 0.00
	Storm 6(04/10/2022)	55.1 ± 0.00	71.8 ± 0.00	86.5 ± 0.00	97.5 ± 0.00
	Mean ± Std. Dev.	68.0 ± 18.3	113 ± 31.2	132 ± 47.2	126 ± 36.2

^a Composite at LID outlet was made of 5 samples.

*No composite data was analyzed for LID Outlet because of technical failure in ISCO at this junction.

Table 13: Percent reductions in average of composite EMC triplicates of TSS and TDS collected in all 6 storms.

Storm ID	Overall Treatment Train		LID Inlet → LID Outlet		LID Outlet → Biochar		Biochar → RemBind	
	TSS	TDS	TSS	TDS	TSS	TDS	TSS	TDS
1	96.6	-140	82.3	-93.0	70.7	-25.2	33.9	0.40
2	87.0	-160	74.0	-158	76.2	-5.10	-105	4.50
3	96.6	-104	N/A*	N/A*	N/A*	N/A*	58.9	1.00
4	94.3	-40.5	98.1 ^a	-48.7 ^a	-141 ^a	1.36 ^a	-25.8	4.20
5	85.4	-51.1	77.8	-28.2	37.1	-24.3	-5.00	5.20
6	84.0	-75.5	81.1	-55.3	28.0	-14.7	-17.9	1.50
p-value ($\alpha = 0.05$)	0.02	0.003	0.04	0.007	>0.05	0.05	>0.05	0.01

^a Composite at LID outlet was made of 5 samples.

*Since LID outlet did not have any composite, percent reductions were not evaluated

Key takeaways for TSS and TDS analysis include:

- 1) Average influent TSS concentrations generally range between 22.9 and 230 mg/L.
- 2) Average effluent TSS concentrations generally range between 1.3 and 14.2 mg/L.
- 3) The overall treatment system yielded significant reductions in TSS event mean concentrations, ranging from 84% to 97% across the six monitored storms.
- 4) Bioretention removed the greatest amount of TSS, with more than 70% reductions achieved at the LID outlet.
- 5) The treatment train system yielded increase in TDS concentration, ranging between 41% and 160% percent increases. There is sufficient evidence that mean composite TDS concentration increases after LID outlet ($p < 0.05$), and thus, bioretention cell is suspected to be a major contributor to TDS increase, ranging between 28% and 158%.
- 6) Statistical analysis showed convincing evidence ($p < 0.05$) that RemBind reduced TDS concentrations at the effluent of overall treatment after the biochar treatment. Removal efficiency ranges from 0.40% to 5.20%.

Alkalinity, COD, and Nutrients

System performance was also assessed for total phosphorus, orthophosphate, total nitrogen, TKN, NO_x (Nitrate + Nitrite), and chemical oxygen demand (COD), total hardness and alkalinity. Figure 6 and Table 8 provide visual and statistical summary of event mean concentrations (EMC) of these water quality parameters, at multiple junctions of the treatment train. Table 9 reports the percent reductions in EMCs of the water quality parameters for the entire treatment train, as well as reductions obtained at multiple stages of the train (i.e., LID inlet to LID outlet, LID outlet to outlet of Biochar cell, outlet of Biochar cell to outlet of Rembind cell).

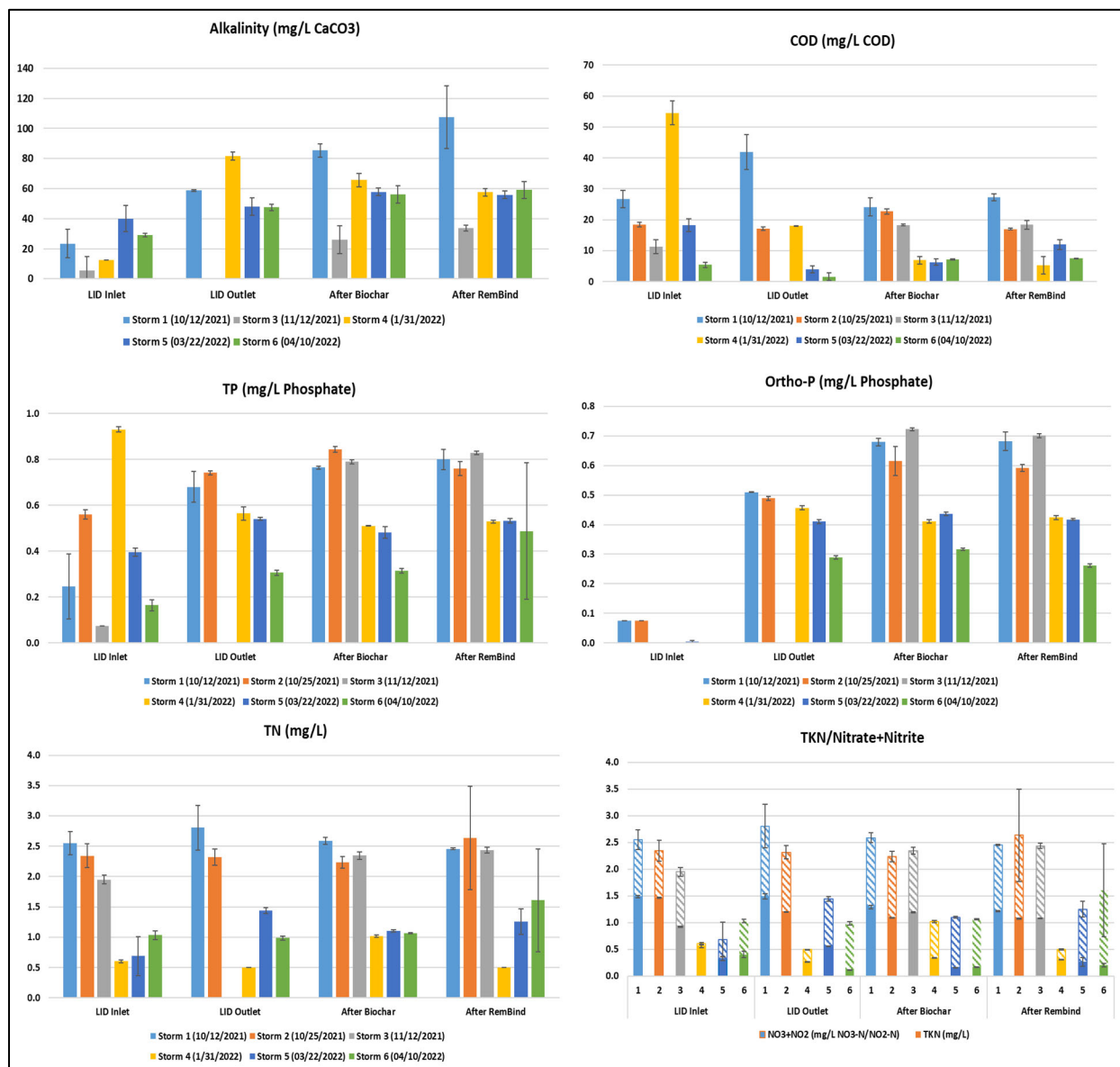


Figure 57: Graphical performance summary for alkalinity, total phosphorus, orthophosphate, total nitrogen, TKN, NO_x (nitrate+nitrite), and chemical oxygen demand (COD). Error bar represents the variability between composite triplicates.

Table 14: Statistical summary of composite triplicates with respect to EMCs of alkalinity, chemical oxygen demand (COD), total phosphorus, orthophosphate, total nitrogen, NO_x (nitrate+nitrite), and Total Kjeldahl Nitrogen (TKN)

Parameter	Storm ID	Location			
		LID Inlet	LID Outlet	After Biochar	After RemBind
Alkalinity (mg/L CaCO ₃)	1	23.4 ± 9.45	58.8 ± 0.60	85.3 ± 4.37	107 ± 20.8
	2	281 ± 2.65	658 ± 31.3	774 ± 35.8	778 ± 31.2
	3	5.37 ± 9.30	-	26.0 ± 9.16	33.6 ± 1.96
	4	12.5	81.8 ^a ± 2.67	65.6 ± 4.46	57.5 ± 2.40
	5	40.0 ± 8.64	47.9 ± 5.72	57.9 ± 2.40	55.9 ± 2.35
	6	29.0 ± 1.15	47.5 ± 2.23	56.1 ± 5.80	59.0 ± 5.60
	Mean ± Std. Dev.	22.1 ± 13.6	59.0 ± 16.1	58.2 ± 21.4	62.7 ± 27.1
COD (mg/L)	1	26.7 ± 2.83	41.9 ± 5.66	24.1 ± 2.84	27.2 ± 1.07
	2	18.4 ± 0.76	17.2 ± 0.55	22.7 ± 0.91	17.0 ± 0.21
	3	11.2 ± 2.27	-	18.3 ± 0.35	18.3 ± 1.42
	4	54.4 ± 3.86	18.0 ^a ± 0.06	6.93 ± 1.20	5.33 ± 2.80
	5	18.3 ± 2.12	3.93 ± 1.10	6.29 ± 0.95	12.0 ± 1.55
	6	5.40 ± 0.87	1.60 ± 1.15	7.10 ± 0.17	7.43 ± 0.06
	Mean ± Std. Dev.	22.4 ± 17.3	16.5 ± 16.0	14.2 ± 8.40	14.6 ± 8.04
TP (mg/L P)	1	0.25 ± 0.14	0.68 ± 0.07	0.76 ± 0.01	0.80 ± 0.04
	2	0.56 ± 0.02	0.74 ± 0.01	0.84 ± 0.01	0.76 ± 0.03
	3	0.08	-	0.79 ± 0.01	0.83 ± 0.01
	4	0.93 ± 0.01	0.56 ^a ± 0.03	0.51	0.53 ± 0.01
	5	0.40 ± 0.02	0.54 ± 0.01	0.48 ± 0.02	0.53 ± 0.01
	6	0.16 ± 0.02	0.31 ± 0.01	0.31 ± 0.01	0.49 ± 0.30
	Mean ± Std. Dev.	0.40 ± 0.31	0.57 ± 0.17	0.62 ± 0.21	0.66 ± 0.16
	1	0.08	0.51	0.68 ± 0.01	0.68 ± 0.03

Ortho-P (mg/L P)	2	0.08	0.49 ± 0.01	0.61 ± 0.05	0.59 ± 0.01
	3	0.00	-	0.72 ± 0.01	0.70 ± 0.01
	4	0.00	0.46 ^a ± 0.01	0.41 ± 0.01	0.42 ± 0.01
	5	0.01	0.41 ± 0.01	0.44 ± 0.01	0.42
	6	0.00	0.29 ± 0.01	0.32	0.26 ± 0.01
	Mean ± Std. Dev.	0.03 ± 0.04	0.43 ± 0.09	0.53 ± 0.16	0.51 ± 0.17
TN (mg/L N)	1	2.55 ± 0.19	2.80 ± 0.37	2.59 ± 0.06	2.46 ± 0.02
	2	2.34 ± 0.20	2.32 ± 0.13	2.23 ± 0.10	2.63 ± 0.85
	3	1.95 ± 0.07	-	2.35 ± 0.06	2.44 ± 0.05
	4	0.60 ± 0.02	0.50 ^a	1.02 ± 0.02	0.50
	5	0.69 ± 0.32	1.44 ± 0.05	1.10 ± 0.02	1.25 ± 0.21
	6	1.03 ± 0.07	0.99 ± 0.03	1.06 ± 0.01	1.61 ± 0.84
	Mean ± Std. Dev.	1.53 ± 0.86	1.61 ± 0.95	1.73 ± 0.74	1.81 ± 0.84
NO3 (mg/L N)	1	1.45 ± 0.02	1.48 ± 0.05	1.43 ± 0.4	1.19 ± 0.01
	2	1.43 ± 0.01	1.20 ± 0.01	1.10	1.07 ± 0.01
	3	0.91 ± 0.01	-	1.20 ± 0.02	1.08 ± 0.01
	4	0.48 ± 0.03	0.26	0.33	0.30 ± 0.01
	5	0.29 ± 0.03	0.55	0.15 ± 0.01	0.26 ± 0.08
	6	0.39 ± 0.06	0.11	0.16 ± 0.01	0.20 ± 0.03
	Mean ± Std. Dev.	1.26 ± 0.30	1.33 ± 0.21	1.18 ± 0.09	1.10 ± 0.07
NO2 (mg/L N)	1	0.03	0.01	0.03	0.03
	2	0.04 ± 0.01	0.02	0.01	0.02
	3	0.01		0.02	0.02
	4	0.08	0.01 ^a	0.01	0.01
	5	0.03	0.01	0.01	0.01
	6	0.02	0.01	0.01	0.01

	Mean ± Std. Dev.	0.03 ± 0.02	0.01 ± 0.01	0.02 ± 0.01	0.02 ± 0.01
TKN (mg/L N)	1	1.07 ± 0.18	1.31 ± 0.41	1.30 ± 0.09	1.24 ± 0.01
	2	0.88 ± 0.19	1.11 ± 0.13	1.14 ± 0.10	1.56 ± 0.86
	3	1.03 ± 0.08	-	1.15 ± 0.06	1.35 ± 0.05
	4	0.04 ± 0.02	0.23 ^a	0.68 ± 0.02	0.19 ± 0.01
	5	0.36 ± 0.32	0.88 ± 0.04	0.94 ± 0.02	0.99 ± 0.15
	6	0.63 ± 0.03	0.86 ± 0.03	0.89 ± 0.01	1.40 ± 0.87
	Mean ± Std. Dev.	0.67 ± 0.40	0.88 ± 0.41	1.02 ± 0.22	1.12 ± 0.49

^aComposite at LID outlet was made of 5 samples.

*No composite data was analyzed for LID Outlet because of technical failure in ISCO at this junction.

Table 15: Percent reductions in average of composite EMC triplicates of Orthophosphate, Total Phosphorus, COD, and Alkalinity collected in all 6 storms + p-value (paired t-test with alpha = 0.05).

Storm ID	Overall Treatment Train		LID Inlet → LID Outlet		LID Outlet → Biochar		Biochar → RemBind	
	Ortho-P	TP	Ortho-P	TP	Ortho-P	TP	Ortho-P	TP
1	-809	-224	-579	-175	-33.2	-12.5	-0.442	-4.62
2	-688	-35.8	-551	-32.3	-25.9	-13.9	3.90	9.95
3	<<0	-1005	N/A*	N/A*	N/A*	N/A*	2.91	-4.98
4	<<0	43.2	<<0 ^a	39.3 ^a	10.1 ^a	9.62 ^a	-3.17	-3.59
5	-8247	-34.9	-8100	-36.9	-6.30	10.9	4.28	-10.7
6	<<0	-196.3	<<0	-86.2	-9.30	-2.72	17.2	-54.9
p-value (α = 0.05)	<0.001	>0.05	<0.001	>0.05	>0.05	>0.05	>0.05	>0.05

Storm ID	Overall Treatment Train		LID Inlet → LID Outlet		LID Outlet → Biochar		Biochar → RemBind	
	COD	Alkalinity	COD	Alkalinity	COD	Alkalinity	COD	Alkalinity
1	-2.13	-359	-57.2	-151	42.4	-45.1	-12.8	-25.9
2	7.66	-145 ^b	6.79	-132 ^b	-32.0	-4.80	25.0	0.00
3	-63.0	-527	N/A*	N/A*	N/A*	N/A*	-63.0	-527
4	86.4	-360	63.8 ^a	-554 ^a	46.3 ^a	19.7 ^a	30.1	12.4
5	33.7	-40.0	70.5	-19.7	-39.6	-20.7	-61.0	3.30
6	-27.5	-104	73.0	-64.0	-366	-18.1	-1.30	-5.20
p-value (α = 0.05)	>0.05	0.01	>0.05	0.04	>0.05	>0.05	>0.05	>0.05

^a Composite at LID outlet was made of 5 samples.

*No composite data was analyzed for LID Outlet because of technical failure in ISCO at this junction.

Key takeaways on nutrients, COD, alkalinity:

- 1) LID bioretention cell generally contributed to increase in total kjeldahl nitrogen (i.e., organic and ammonia nitrogen) ($p = 0.004$), orthophosphate ($p < 0.001$), and alkalinity ($p < 0.05$). However, for total phosphorus, inorganic nitrogen ($\text{NO}_3 + \text{NO}_2$ nitrogen), COD, and total nitrogen, LID cell fluctuated in performance across storms, leading to reduction in averages of composite EMC triplicates sometimes versus increase or no change at

other times. Additionally, the hydrological conditions such as amount of preceding dry days and sampled storm duration did not show any correlation between these fluctuations.

- a. Increases in total phosphorus have also been reported in other studies, including those recorded in the BMP Database 2020 Performance Summary: “leaching of phosphorus from soils/planting media and resuspension of captured particulate phosphorus may be a cause of phosphorus increases observed in vegetated BMPs such as bioretention, swales, and filter strips” (Clary et al. 2020).
 - b. Variability in dominance of nitrification (aerobic process) and denitrification (anaerobic process) processes in the LID cell are potential causes of observed increases and decreases in nitrogen. This has also been reported in other studies, such as Wang et al. (2017).
- 2) Biochar did not affect the EMCs of total phosphorus, alkalinity, total nitrogen, inorganic nitrogen, and orthophosphates ($p > 0.05$). It may seem that biochar contributed to the reduction of COD; however, the reductions varied from -366% increase to 42% removal efficiency and the difference was not found to be statistically significant ($p > 0.05$). Studies conducted on biochar mixtures with soil have estimated COD reduction by more than 80% (Sang et al., 2019), but this study indicated the maximum removal efficiency of only 42% when biochar was 6 months and 14 days old and showed growing decline in performance over time. Moreover, a strong correlation between biochar age and decrease in percent reductions of COD concentrations was determined (spearman’s rank correlation coefficient $r = -1.0$). The typical COD concentrations of receiving surface water observed to equal less than 200 mg/L and less than 20 mg/L of unpolluted water bodies (Jain & Singh, 2003). The COD effluent after biochar, however, showed concentrations within the range of uncontaminated surface water resources.
- 3) Rembind, similar to Biochar, did not affect the EMCs of total phosphorus, alkalinity, total nitrogen, inorganic nitrogen, and orthophosphates ($p > 0.05$).
- 4) Total alkalinity increases at the end of treatment; however, major increases occurred in the LID cell and before the biochar cell in the treatment train.
 - a. Note that the alkalinity of the second storm was found to be, on average, much greater than 100 mg/L for every monitored location. However, the other storms were found to have alkalinity concentration below or around 100 mg/L (see Figure 58 a & b for details). Additionally, pH remained close to 7.0 for the monitored locations during storm 2. Alkalinity indicates the water body’s capacity to neutralize acids and bases, and thus, a more stable pH is indicative of high alkalinity. Since the trends in the alkalinity for Storm 2 do seem to follow the levels of alkalinity observed during Storms 1 and 3, we assumed the catchment area (i.e., the county’s maintenance and service facility) could be the major source of chemicals leading to high alkalinity in the inflow. However, facility staff were not aware of any evidence of limestone presence or similar material between 10/13/2021 and 10/25/2021, hence this assumption was not verified.

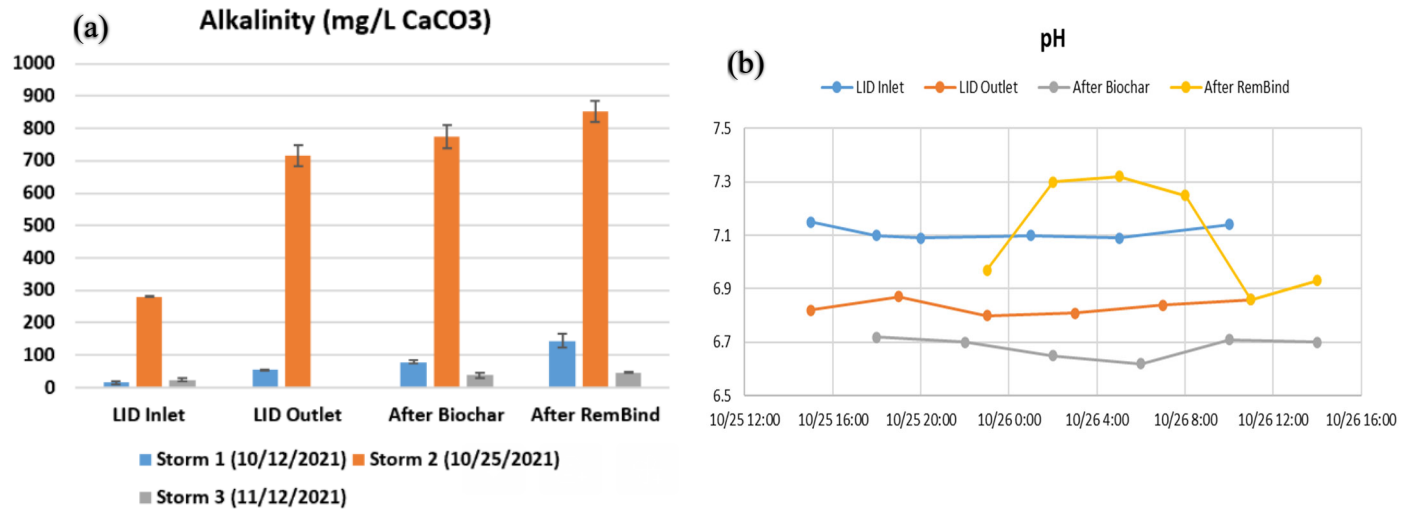


Figure 58: (a) High alkalinity concentration during storm 2; (b) pH observations for storm 2.

Heavy Metals

System performance was assessed for heavy metals, including copper and zinc. Figure 59 and Table 16 provide visual and statistical summary of event mean concentrations (EMC) of these water quality parameters, at multiple junctions of the treatment train.

Table 17 reports the percent reductions in EMCs of the water quality parameters for the entire treatment train, as well as reductions obtained at multiple stages of the train (i.e., LID inlet to LID outlet, LID outlet to outlet of Biochar cell, outlet of Biochar cell to outlet of Rembind cell).

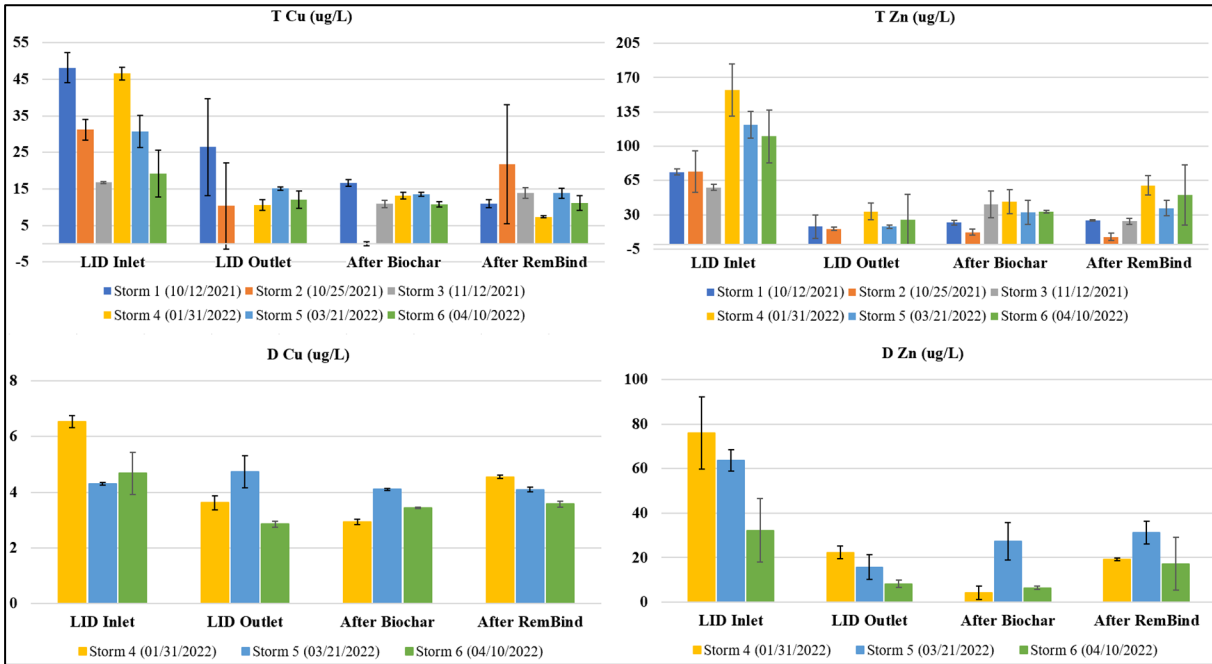


Figure 59: Graphical performance summary for total copper and total zinc. Error bar represents the variability between composite triplicates.

Table 16: Statistical summary of composite triplicates with respect to EMCs of total copper and total zinc.

Parameter	Storm ID (Date)	LID Inlet	LID Outlet	After Biochar	After RemBind
Total Zn (µg/L)	Storm 1 (10/12/2021)	73.6 ± 3.20	17.9 ± 11.9	22.1 ± 2.38	24.4 ± 0.73
	Storm 2 (10/25/2021)	74.1 ± 21.5	15.7 ± 1.52	12.3 ± 3.03	7.50 ± 3.84
	Storm 3 (11/12/2021)	58.0 ± 3.09	-	40.6 ± 13.8	23.3 ± 2.91
	Storm 4 (01/31/2022)	157 ± 26.8	33.4 ^a ± 8.48	43.4 ± 12.1	60.1 ± 9.90
	Storm 5 (03/22/2022)	122 ± 13.9	17.9 ± 1.85	32.6 ± 12.4	36.8 ± 7.96
	Storm 6(04/10/2022)	110 ± 26.8	25.3 ± 25.7	33.1 ± 1.60	50.4 ± 30.8
	Mean ± Std. Dev.	99.1 ± 37.4	22.1 ± 7.31	30.7 ± 11.7	33.8 ± 19.3
Total Cu (µg/L)	Storm 1 (10/12/2021)	48.1 ± 4.12	26.5 ± 13.3	16.6 ± 0.92	11.0 ± 1.14
	Storm 2 (10/25/2021)	31.2 ± 2.84	10.4 ± 11.9	0.00 ± 0.60	21.8 ± 16.3
	Storm 3 (11/12/2021)	16.8 ± 0.27	-	10.9 ± 1.04	13.9 ± 1.52
	Storm 4 (01/31/2022)	46.6 ± 1.74	10.6 ^a ± 1.40	13.1 ± 0.94	7.40 ± 0.26
	Storm 5 (03/22/2022)	30.7 ± 4.40	15.1 ± 0.42	13.5 ± 0.54	13.8 ± 1.35

	Storm 6(04/10/2022)	19.2 ± 6.36	12.0 ± 2.36	10.8 ± 0.75	11.2 ± 1.98
	Mean ± Std. Dev.	32.1 ± 13.2	14.9 ± 6.73	10.8 ± 5.71	13.2 ± 4.85
Dissolv. Zn (µg/L)	Storm 1 (10/12/2021) ^b	42.8 ± 2.41	68.2 ± 15.4	59.9 ± 2.87	40.2 ± 10.3
	Storm 2 (10/25/2021) ^b	45.9 ± 3.45	51.6 ± 2.56	40.8 ± 4.74	37.6 ± 3.80
	Storm 3 (11/12/2021) ^b	51.8 ± 2.06	-	47.4 ± 4.91	33.0 ± 3.06
	Storm 4 (01/31/2022)	76.0 ± 16.4	22.3 ^a ± 2.89	4.19 ± 2.95	19.2 ± 0.52
	Storm 5 (03/22/2022)	63.7 ± 4.78	15.7 ± 5.46	27.4 ± 8.35	31.3 ± 5.11
	Storm 6(04/10/2022)	32.3 ± 14.2	8.16 ± 1.66	6.46 ± 0.71	17.2 ± 11.8
	Mean ± Std. Dev.	57.3 ± 22.2	15.4 ± 9.37	12.7 ± 10.9	22.6 ± 7.64
Dissolv. Cu (µg/L)	Storm 1 (10/12/2021) ^b	13.8 ± 12.1	12.5 ± 0.11	10.1 ± 1.28	4.36 ± 0.15
	Storm 2 (10/25/2021) ^b	6.05 ± 2.34	8.38 ± 0.13	6.96 ± 0.11	7.54 ± 0.31
	Storm 3 (11/12/2021) ^b	3.49 ± 0.02	-	6.36 ± 0.19	7.33 ± 0.13
	Storm 4 (01/31/2022)	6.54 ± 0.21	3.62 ^a ± 0.25	2.93 ± 0.09	4.56 ± 0.06
	Storm 5 (03/22/2022)	4.31 ± 0.05	4.74 ± 0.57	4.10 ± 0.03	4.10 ± 0.09
	Storm 6(04/10/2022)	4.68 ± 0.76	2.85 ± 0.11	3.44 ± 0.02	3.57 ± 0.10
	Mean ± Std. Dev.	5.20 ± 0.99	3.74 ± 0.66	3.50 ± 0.02	4.08 ± 0.50

Table 17: Percent reductions in average of composite EMC triplicates of total (T) and dissolved (D) copper (Cu) and zinc (Zn) collected in all 6 storms + p-value (paired t-test with alpha = 0.05).

Storm ID	Overall Treatment Train		LID Inlet → LID Outlet		LID Outlet → Biochar		Biochar → RemBind	
	T Cu	D Cu	T Cu	D Cu	T Cu	D Cu	T Cu	D Cu
1	77.2	-	45.0	-	70.7	-	33.8	-
2	30.2	-	66.8	-	76.2	-	<<0	-
3	17.3	-	N/A*	N/A*	N/A*	N/A*	-27.5	-
4	84.1	30.4	77.2 ^a	44.7 ^a	-23.6 ^a	19.0 ^a	43.6	-55.4
5	55.0	4.9	50.7	-10.0	10.5	13.5	-2.1	0.00
6	41.6	23.7	37.3	39.1	10.2	-20.5	-3.7	-4.00
p-value (α = 0.05)	0.015	>0.05	0.006	>0.05	>0.05	>0.05	>0.05	>0.05

Storm ID	Overall Treatment Train		LID Inlet → LID Outlet		LID Outlet → Biochar		Biochar → RemBind	
	T Zn	D Zn	T Zn	D Zn	T Zn	D Zn	T Zn	D Zn
1	66.8	-	75.6	-	-23.4	-	-10.3	-
2	89.9	-	78.8	-	22.0	-	39.0	-
3	59.8	-	N/A*	N/A*	N/A*	N/A*	42.6	-
4	61.8	74.8	78.8 ^a	70.6 ^a	-30.0 ^a	81.2 ^a	-38.3	-358
5	69.8	50.8	85.3	75.3	-82.2	-74.3	-13.0	-14.2
6	54.2	46.6	77.0	74.7	-31.1	20.8	-52.1	-167
p-value (α = 0.05)	0.05	<0.001	0.02	0.001	>0.05	0.05	>0.05	>0.05

Key takeaways on total copper and zinc:

- 1) Overall, the treatment train reduced total copper and total zinc by 17% - 84% and 54% - 90%, respectively. For three monitored storms, the treatment train was also consistent in

removing dissolved copper by modest amount (5% - 30%) and dissolved zinc by 47% - 75%.

- 2) The bioretention cell efficiently removes total copper (37% - 77%) and total zinc (76% - 85%) being the major contributor to heavy metal removal within the treatment train. The dissolved copper was exported from the bioretention cell during storm 4, but the other two storms showed the removal efficiency of 39% - 45%. The bioretention cell demonstrated a constant removal efficiency of dissolved zinc by more than 70% ($p < 0.001$). The overall treatment train treatment and bioretention cell indicated a significant reduction of total copper and total and dissolved zinc.
- 3) Biochar further reduced total copper exported from LID by 10% - 70%; however, this reduction was not found statistically significant. Additionally, for storms where Biochar contributed to reductions, dissolved copper was reduced by 14% - 19% and dissolved zinc was reduced by 21% - 81%. However, the biochar started to export dissolved copper (-21%) during the sampling of storm 6 and dissolved zinc (-74%) during storm 5 suggesting a decrease in performance over time. An inconsistency in treatment of total zinc was observed by reduction of 22% in storm 2, while all other storms experienced an increase in total zinc ranging from 23% - 82%; hence, the increase in total zinc during biochar treatment was not significant ($p > 0.05$). Although the effluent treated by biochar did not significantly increase in total copper and zinc concentrations, the strong correlation of decrease in biochar performance and biochar age was observed (spearman's rank correlation coefficient $r = -0.92$).
- 4) RemBind removed total copper at the beginning of the monitoring period, and also contributed to remediation of total copper when it was exported by biochar during storm 4. As the RemBind aged, the analyzed metals experienced increases though total zinc had a removal of 39% - 42% for storms 2 and 3. The non-parametric spearman's rank correlation coefficient resulted in strong negative association ($r = -1.0$) between RemBind age and the percent reductions of total zinc.

Polycyclic Aromatic Hydrocarbons (PAHs)

System performance was assessed for parent polycyclic aromatic hydrocarbons (PAHs), of which 20 common, mostly parent PAHs were used as a baseline for PAH presence (see

Table 18 for individual compounds). For the first three of the above storm events, field sample composites (~400 mL each) were collected in triplicate from each of the four junction outflows using the ISCO samplers, as above.

Samples were refrigerated at 4 °C and were denatured with 25% v/v acetonitrile. Prior to sampling, bottles had 150 uL of nominal 2.2 ng/uL solution of mixed, isotopically labeled surrogate added to each bottle.

Stormwater Solid Phase Extraction

Samples were processed using a modified solid phase extraction protocol intended to remove humic acids and other dissolved solids while retaining PAHs from stormwater (Aqeel et al. 2010). A multi-port SPE vacuum manifold was utilized and prepared prior to use by sonication soaking all fittings with MeOH, ethyl acetate, and hexanes. Phenomenex Strata[®] PAH SPE cartridges were conditioned (eluted 3x column volumes [CV, approximately 6 mL; ~18 mL total] of each solvent: DCM, MeOH, and DI water) prior to loading sample dropwise onto SPE cartridges utilizing siphon tubing, polyethelyne, and stainless-steel fittings. Following loading, cartridges were then washed with one CV 1:1 MeOH/water solution and air dried for 15 seconds. Samples were eluted with 3x CV of DCM and collected in washed and baked 40 mL amber glass vials. Vials had ~ 5 g of trace-PAH graded NaSO₄ drying agent added to sequester water in the sample, vigorously shaken, let settle, and the supernatant decanted into secondary tared 40 mL vial. Samples were evaporated under N₂ ENEVAP apparatus, transferred to 2 mL autosampler vial inserts (~ 300 uL) with a single rinse transfer, further dried under stream of N₂ to 150 uL, and had 50 uL internal standard (ISTD, nominal 2.0 ng/uL; mix of three deuterated-PAHs). Final volume of 200 uL sample was analyzed on GCMS under the conditions below.

GC/MS Methods

PAH samples were analyzed on an Agilent 6890 gas chromatograph (GC) coupled to a 5973 mass spectrometer (MS) based on Trine et al., 2019. The analysis was conducted in electron ionization (EI) in selective ion monitoring (SIM) mode, using a DB-5MS (Agilent, 30 m × 0.25 mm i.d., 0.25 µm film thickness) GC column. PAH data below was obtained in SIM mode but samples were also analyzed in full scan mode (full scan data not applicable at this time).

Further GC/MS conditions were as follows: the inlet was operated in splitless mode and the inlet and interface temperatures were maintained at 300 °C and 320 °C, respectively. Helium was used as the carrier gas at 1.0 mL min⁻¹. The oven temperature program was as follows: initial temperature 60 °C held for 1 min, ramped at 6 °C min⁻¹ until 210 °C, held for 2 min, ramped at 6 °C min⁻¹ until 300 °C, held for 2 min, ramped at 40 °C until 320 °C, and held for 1.5 min for a total run time of 47 min. The ion source and quadrupole were set to 230 °C and 150 °C, respectively.

Commercially available isotopically labelled standards were used to quantify all parent PAHs in

Table 18—**Error! Reference source not found..** Methods and standards were used as in Trine et al. 2019 and reported in quantities of pg PAH per mL of stormwater sampled (pg/mL). SIM method parameters for the MS method program, including windows, fragment ions, and retention times, are based on prior research as found in Trine et al., 2019. The limits of detection (LOD) and limits of quantitation (LOQ) were found by analyzing replicate control standards ($n = 8$), and by calculating the LOD as $(3 \cdot s)/m$ and LOQ as $(10 \cdot s)/m$, where m is the average response for each analyte and s is the standard deviation for each analyte. Calculation adjustments were made for the final pg/mL sample amount for both samples and LOD/LOQ values based on averages of background signal from combined stormwater for each sample and storm, as in

Table 18–Table 20, with LOD/LOQ values in

Table 21**Error! Reference source not found..** Table S 1–Table S 4 (see Appendix) are reorganized for comparing sampling location between storms.

Table 18: Parent PAHs in Storm 1.

PAH (pg/mL) $\pm$ std. err. of μ	Storm 1 - 10/12/2021			
	LID Inlet	LID Outlet	After Biochar	After RemBind
Naphthalene	1.20 $\pm$ 0.43	< LOD	0.32 $\pm$ 0.23	0.91 $\pm$ 0.46
Acenaphthylene	< LOD	< LOD	< LOD	< LOD
Acenaphthene	< LOD	< LOD	< LOD	< LOD
Fluorene	< LOD	< LOD	< LOD	< LOD
Phenanthrene	1.69 $\pm$ 0.28	0.64 $\pm$ 0.13	< LOD	< LOQ
Anthracene	< LOD	< LOD	< LOD	< LOD
Fluoranthene	5.25 $\pm$ 0.94	18.35 $\pm$ 7.67	1.70 $\pm$ 1.25	3.88 $\pm$ 3.17
Pyrene	5.82 $\pm$ 1.19	27.22 $\pm$ 10.11	1.65 $\pm$ 1.59	3.51 $\pm$ 2.72
Retene	4.61 $\pm$ 0.76	17.36 $\pm$ 7.43	1.62 $\pm$ 1.67	3.30 $\pm$ 3.05
Benz(c)fluorene	0.44 $\pm$ 8.43	12.41 $\pm$ 9.12	0.64 $\pm$ 8.59	0.73 $\pm$ 8.67
Benzo(a)anthracene	< LOD	< LOD	< LOD	< LOD
Chrysene+Triphenylene	7.59 $\pm$ 1.54	24.09 $\pm$ 9.89	2.83 $\pm$ 2.11	4.54 $\pm$ 3.91
Benzo(b)fluoranthene	2.99 $\pm$ 0.07	7.19 $\pm$ 2.86	1.07 $\pm$ 0.90	1.86 $\pm$ 1.62
Benzo(k)fluoranthene	1.99 $\pm$ 0.28	6.34 $\pm$ 2.60	< LOD	1.40 $\pm$ 1.22
Benzo(e)pyrene	3.65 $\pm$ 0.16	5.76 $\pm$ 2.32	< LOD	< LOD
Benzo(a)pyrene	< LOD	< LOD	< LOD	< LOD
Indeno(1,2,3-cd)pyrene	< LOD	< LOD	< LOD	< LOD
Dibenz(a,h)+(a,c)anthracene	< LOD	< LOD	< LOD	< LOD
Benzo(ghi)perylene	< LOD	< LOD	< LOD	< LOD

Table 19: Parent PAHs in Storm 2.

PAH (pg/mL) $\pm$ std. err. of μ	Storm 2 - 10/25/2021			
	LID Inlet	LID Outlet	After Biochar	After RemBind
Naphthalene	< LOD	< LOD	< LOD	< LOD
Acenaphthylene	< LOD	< LOD	< LOD	< LOD
Acenaphthene	< LOD	< LOD	< LOD	< LOD
Fluorene	< LOD	< LOD	< LOD	< LOD
Phenanthrene	< LOD	< LOD	< LOD	< LOD
Anthracene	< LOD	< LOD	< LOD	< LOD
Fluoranthene	1.75 $\pm$ 0.34	< LOD	< LOD	< LOD
Pyrene	16.29 $\pm$ 11.18	1.68 $\pm$ 1.97	< LOD	7.26 $\pm$ 4.93
Retene	< LOQ	< LOD	< LOD	< LOD
Benz(c)fluorene	20.06 $\pm$ 8.19	9.91 $\pm$ 8.09	< LOD	< LOD
Benzo(a)anthracene	< LOQ	< LOD	< LOD	< LOD
Chrysene+Triphenylene	4.15 $\pm$ 0.32	1.57 $\pm$ 0.85	< LOD	0.72 $\pm$ 1.00
Benzo(b)fluoranthene	2.36 $\pm$ 0.39	0.94 $\pm$ 0.38	< LOD	< LOQ
Benzo(k)fluoranthene	0.96 $\pm$ 0.23	0.74 $\pm$ 0.27	< LOD	< LOQ
Benzo(e)pyrene	< LOD	0.77 $\pm$ 0.32	< LOD	< LOQ
Benzo(a)pyrene	< LOD	< LOD	< LOD	< LOD
Indeno(1,2,3-cd)pyrene	12.48 $\pm$ 10.19	< LOD	< LOD	< LOD
Dibenz(a,h)+(a,c)anthracene	14.47 $\pm$ 11.82	14.78 $\pm$ 12.07	< LOD	< LOD
Benzo(ghi)perylene	8.99 $\pm$ 3.67	< LOD	< LOD	< LOD

Table 20: Parent PAHs in Storm 3.

PAH (pg/mL) $\pm$ std. err. of μ	Storm 3 - 11/12/2021			
	LID Inlet	LID Outlet	After Biochar	After RemBind
Naphthalene	< LOD	NA	< LOD	3.00 $\pm$ 5.12
Acenaphthylene	< LOD		< LOD	< LOD
Acenaphthene	< LOD		< LOD	< LOD
Fluorene	< LOD		1.57 $\pm$ 13.72	< LOD
Phenanthrene	7.37 $\pm$ 4.95		3.32 $\pm$ 1.75	6.98 $\pm$ 11.89
Anthracene	8.47 $\pm$ 10.44		< LOD	< LOD
Fluoranthene	1.45 $\pm$ 0.83		2.01 $\pm$ 3.74	0.46 $\pm$ 1.20
Pyrene	1.48 $\pm$ 0.86		1.72 $\pm$ 2.05	0.53 $\pm$ 1.54
Retene	< LOD		1.84 $\pm$ 3.93	1.61 $\pm$ 1.75
Benz(c)fluorene	< LOD		< LOD	< LOD
Benzo(a)anthracene	< LOD		< LOD	< LOD
Chrysene+Triphenylene	3.97 $\pm$ 0.80		4.77 $\pm$ 4.02	< LOD
Benzo(b)fluoranthene	7.23 $\pm$ 5.89		14.07 $\pm$ 1.03	< LOD
Benzo(k)fluoranthene	1.96 $\pm$ 1.69		3.92 $\pm$ 0.72	< LOD
Benzo(e)pyrene	3.97 $\pm$ 3.09		7.08 $\pm$ 0.33	< LOD
Benzo(a)pyrene	< LOD		< LOD	< LOD
Indeno(1,2,3-cd)pyrene	< LOD		< LOD	< LOD
Dibenz(a,h)+(a,c)anthracene	< LOD		< LOD	< LOD
Benzo(ghi)perylene	< LOD		< LOD	< LOD

Table 21: Parent PAHs limits of detection (LOD) and quantitation (LOQ).

PAH (pg/mL)	LOD	LOQ
Naphthalene	0.08	0.25
Acenaphthylene	0.08	0.26
Acenaphthene	0.03	0.09
Fluorene	0.03	0.10
Phenanthrene	0.04	0.13
Anthracene	0.07	0.23
Fluoranthene	0.04	0.14
Pyrene	0.05	0.18
Retene	0.11	0.37
Benz(c)fluorene	0.11	0.36
Benzo(a)anthracene	0.19	0.62
Chrysene+Triphenylene	0.11	0.37
Benzo(b)fluoranthene	0.21	0.71
Benzo(k)fluoranthene	0.14	0.48
Benzo(e)pyrene	0.20	0.65
Benzo(a)pyrene	0.09	0.31
Indeno(1,2,3-cd)pyrene	0.14	0.45
Dibenz(a,h)+(a,c)anthracene	0.13	0.44
Benzo(ghi)perylene	0.17	0.56

Discussion

Individual sample and PAH variation combined with storm to storm variation in analyte recovery suggests little consistent trend of PAHs in the stormwater samples. The standard mean error for each of the triplicate sampling events suggest high variability and low confidence in understanding the sorbency potential of PAHs in the treatment train.

Recoveries of surrogate from SPE sampling were all well within parameters for analysis, and analytical system controls, internal standard, and external system control check samples for GCMS analysis were within laboratory acceptance limits ($\pm 30\%$ reported values). Stormwater field blank samples showed significant PAH signals over system LOD and LOQ that their responses were averaged and subtracted from analyte signals and further incorporated into the final LOD and LOQ values.

Further and sustained data collection from additional and extended storm events would be useful to add to the data and improve statistical significance. Coupling PAH data with flow rates and further system conditions may further help to explain potential of sorbency effects or appearance of PAHs in sections of the treatment train. Further modeling could be beneficial but was outside the scop of this project.

Key takeaways for PAH analysis include:

1. Limited parent PAH concentrations above the detection limits and error were measured.
2. High variability in PAH data prevent significant understanding about sorbency effects.
3. Variations suggest that further testing and replicates may be helpful.
4. Examining field blanks further may help in improving detection and quantitation limits.

Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS)

Since no PFAS was previously detected at the inflow, the treatment train was not evaluated for PFAS removal rates.

Task 4

Task 4.1 – Calibration and Validation of existing SWMM model

Preliminary work on the development and calibration has been completed. Because of delays in the project due to COVID-19, we focused on field data collection on stormwater flows and water quality parameters as part of Task 3.3. The new data collected will inform final remaining tasks related to calibration and validation of existing SWMM model for heavy metals and nutrients, and its comparison with model updates in Task 4.2. Final calibrated and validated model will be included as part of MS student Ms. Alisha Saduova's thesis and undergraduate student's research by end of 2022.

Task 4.2 – Development of new compartment-based model components in SWMM

Task related to UAV-based monitoring approach was completed and are reported in Task 3.3 results, details on the validation of the compartment-based model using this plant data as well as new water quality data from storms sampled in 2021-2022 are not currently available, since it was not completed because of Covid-19 delays and hurdles.

Conclusions and Implications for Future Research and Implementation

Key Points from Task 1

- Five sorbents, including bioswale soil, activated carbon, and high ion exchange capacity materials were tested to determine their removal efficiencies of heavy metals and PFASs under both clean synthetic stormwater conditions and under dirtier collected stormwater conditions.
- Under clean synthetic stormwater conditions, Biochar Basic™ demonstrated superior removal of Cu^{2+} and Zn^{2+} while RemBind® demonstrated the highest removal of PFASs.
- None of the sorbents tested were effective at removing the four carbon PFBA compound.
- Under dirtier collected stormwater conditions, the removal efficiencies of all sorbents for all contaminants decreased. The only exception is the removal of FtSaB by RemBind® and EarthLite™ which stayed the same or slightly increased under the collected stormwater condition.
- Under collected stormwater conditions, all the sorbents demonstrated similar Zn^{2+} and Cu^{2+} removal efficiencies while GAC demonstrated the most consistent PFAS removal, and EarthLite™ and RemBind® showed the highest ability to remove FtSaB.
- The collected stormwater was found to be high in DOC and very high in Fe content which may be the cause for the decreased removal efficiencies by the sorbents.
- The high DOC content in the collected stormwater may bind with Cu^{2+} resulting in Cu^{2+} removal via hydrophobic interactions as opposed to cation exchange.
- The high DOC content in the collected stormwater may also coat the surface of the sorbents reducing the active sites available for cation or anion exchange. Thus, Zn^{2+} and Cu^{2+} removals were reduced and only PFASs with longer carbon chains showed significant removal under these conditions.
- The very high Fe content in the collected stormwater may also interfere with Cu^{2+} and Zn^{2+} removal via direct competition for binding sites.

The data from Task 1 is currently being prepared in a manuscript by Casey Kanalos, a M.S. student under the direction of T. Radniecki at Oregon State University, and Bethany Parker, a Ph.D. student under the direction of J. Field and S. Simonich at Oregon State University.

Key Points from Task 2

- To date, this is the most extensive study found evaluating plant groups for maximum PFAS phytoremediation potential.
- Selected Biochar Basic and Rembind as the best two sorbents for heavy metals and PFAS.
- Demonstrated that synthetic stormwater is not a suitable alternative to real stormwater.

- Found that organic matter played the strongest role in reducing sorbent performance, but had a lesser effect on heavy metals due to complexations.
- Validated that pretreating stormwater with Biochar Basic improves Rembind's removal of PFAS.
- Protein content, transpiration type, root type, stem type, and leaf mass all contribute to uptake and translocation of PFAS.
- Plant selection will vary based on location and water depth; but plant mass and water consumption should factor into decision making along with BCF.
- Anion exchange affinity of PFAS depends on chain length, head group, and -CH- 'spacers'.
- Average electrostatic potential can be used as a proxy for anion exchange affinity.
- Pretreatment of stormwater with Biochar Basic gave significantly greater removal of eleven out of twenty-one PFAS.
- Grasses and stemless dicots demonstrate greatest phytoremediation potential.
- Plant selection depends on treatment variables.
- Mass accumulation factors should be taken into account for plant selection.

Key Points from Task 3

Sediment Tracer Study

- Using tracer study, sediment-borne contaminant load on a per-size-fraction basis were quantified. The results showed contaminant load increased with decreasing particle size, as would be expected due to the larger surface area associated with smaller particles, with one exception of Fe which had greatest contaminant load for sizes 25-75 μm .
- A new model for fine sediment transport in LID-like conditions was developed. The model also allows for representation of the "clogging" effect that occurs when high concentrations of fine sediment are present in the influent stormwater.

Plant Monitoring

- Ground-based monitoring of green infrastructure (GI) facilities for estimation of fraction of intercepted photosynthetically active radiation (fiPAR) poses multiple operational challenges.
- Uninhabited aircraft systems (UAS) were found to enable efficient acquisition of multi-temporal normalized difference vegetation index (NDVI) data for GI site monitoring, through the workflow developed in Prettyman et al. (2020)

Treatment Train Performance

- Turbidity
 - Overall, the treatment train system reduced turbidity from an average of 94 NTU at the influent to an average of 14 NTU at the effluent in the six monitored storms. A tendency of a slight increase in turbidity was, however, observed after Rembind treatment train for all six storms, which could be attributed to leaching fines.

- Residence Time
 - Across 6 storms, residence time of LID was about 90 minutes when the number of antecedent dry days were ≥ 1 . Biochar and Rembind Cells' residence time varied from 10 - 37 minutes.
 - TSS and TDS analysis
 - Average influent TSS concentrations generally range between 22.9 and 230 mg/L.
 - Average effluent TSS concentrations generally range between 1.3 and 14.2 mg/L.
 - The overall treatment system yielded significant reductions in TSS event mean concentrations, ranging from 84% to 97% across the six monitored storms.
 - Bioretention removed the greatest amount of TSS, with more than 70% reductions achieved at the LID outlet.
 - The treatment train system yielded increase in TDS concentration, ranging between 41% and 160% percent increases. There is sufficient evidence that mean composite TDS concentration increases after LID outlet ($p < 0.05$), and thus, bioretention cell is suspected to be a major contributor to TDS increase, ranging between 28% and 158%.
 - Statistical analysis showed convincing evidence ($p < 0.05$) that RemBind reduced TDS concentrations at the effluent of overall treatment after the biochar treatment. Removal efficiency ranges from 0.40% to 5.20%.
- Nutrients, COD, alkalinity
 - LID bioretention cell generally contributed to increase in total Kjeldahl nitrogen (i.e., organic and ammonia nitrogen) ($p = 0.004$), orthophosphate ($p < 0.001$), and alkalinity ($p < 0.05$). However, for total phosphorus, inorganic nitrogen ($\text{NO}_3 + \text{NO}_2$ nitrogen), COD, and total nitrogen, LID cell fluctuated in performance across storms, leading to reduction in averages of composite EMC triplicates sometimes versus increase or no change at other times. Additionally, the hydrological conditions such as amount of preceding dry days and sampled storm duration did not show any correlation between these fluctuations.
 - Increases in total phosphorus have also been reported in other studies, including those recorded in the BMP Database 2020 Performance Summary: "leaching of phosphorus from soils/planting media and resuspension of captured particulate phosphorus may be a cause of phosphorus increases observed in vegetated BMPs such as bioretention, swales, and filter strips."
(https://www.waterrf.org/system/files/resource/2020-11/DRPT-4968_0.pdf)
 - Variability in dominance of nitrification (aerobic process) and denitrification (anaerobic process) processes in the LID cell are potential causes of observed increases and decreases in nitrogen. This has also been reported in other studies, such as Wang et al. (2017).
 - Biochar did not affect the EMCs of total phosphorus, alkalinity, total nitrogen, inorganic nitrogen, and orthophosphates ($p > 0.05$). It may seem that biochar contributed to the reduction of COD; however, the reductions varied from -366% increase to 42% removal efficiency and the difference was not found to be statistically significant ($p > 0.05$). Studies conducted on biochar mixtures with soil have estimated COD reduction by more than 80% (Sang et al., 2019), but this study indicated the maximum removal efficiency of only 42% when biochar was 6 months and 14 days old and showed growing decline in performance over time.

Moreover, a strong correlation between biochar age and decrease in percent reductions of COD concentrations was determined (spearman's rank correlation coefficient $r = -1.0$). The typical COD concentrations of receiving surface water observed to equal less than 200 mg/L and less than 20 mg/L of unpolluted water bodies (Jain & Singh, 2003). The COD effluent after biochar, however, showed concentrations within the range of uncontaminated surface water resources.

- Rembind, similar to Biochar, did not affect the EMCs of total phosphorus, alkalinity, total nitrogen, inorganic nitrogen, and orthophosphates ($p > 0.05$).
- Heavy Metals (Copper and Zinc)
 - Overall, the treatment train reduced total copper and total zinc by 17% -84% and 54% -90%, respectively. For three monitored storms, the treatment train was also consistent in removing dissolved copper by modest amount (5% -30%) and dissolved zinc by 47% - 75%.
 - The bioretention cell efficiently removes total copper (37% -77%) and total zinc (76% -85%) being the major contributor to heavy metal removal within the treatment train. The dissolved copper was exported from the bioretention cell during storm 4, but the other two storms showed the removal efficiency of 39% - 45%. The bioretention cell demonstrated a constant removal efficiency of dissolved zinc by more than 70% ($p < 0.001$). The overall treatment train treatment and bioretention cell indicated a significant reduction of total copper and total and dissolved zinc.
 - Biochar further reduced total copper exported from LID by 10% -70%; however, this reduction was not found statistically significant. Additionally, for storms where Biochar contributed to reductions, dissolved copper was reduced by 14% - 19% and dissolved zinc was reduced by 21% -81%. However, the biochar started to export dissolved copper (-21%) during the sampling of storm 6 and dissolved zinc (-74%) during storm 5 suggesting a decrease in performance over time. An inconsistency in treatment of total zinc was observed by reduction of 22% in storm 2, while all other storms experienced an increase in total zinc ranging from 23% to 82%; hence, the increase in total zinc during biochar treatment was not significant ($p > 0.05$). Although the effluent treated by biochar did not significantly increase in total copper and zinc concentrations, the strong correlation of decrease in biochar performance and biochar age was observed (spearman's rank correlation coefficient $r = -0.92$).
 - RemBind removed total copper at the beginning of the monitoring period, and also contributed to remediation of total copper when it was exported by biochar during storm 4. As the RemBind aged, the analyzed metals experienced increases though total zinc had a removal of 39% - 42% for storms 2 and 3. The non-parametric spearman's rank correlation coefficient resulted in strong negative association ($r = -1.0$) between RemBind age and the percent reductions of total zinc.
- PAH analysis
 - Limited parent PAH concentrations above the detection limits and error were measured.
 - High variability in PAH data prevent significant understanding about sorbency effects.

- Variations suggest that further testing and replicates may be helpful.
- Examining field blanks further may help in improving detection and quantitation limits.

Key Points from Task 4

- Preliminary work on the development and calibration of baseline SWMM model has been completed. However, inclusion of storm data collected in 2021-2022 in the model has not been completed.
- Plan for the compartment-based modeling approach has been identified. However, the computer code has not been tested and validated because of covid-19 delays.

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Appendices

Dissolved Organic Carbon (DOC) — Addendum

Stormwater was collected from the OGSIR stormwater influent. The stormwater was vacuum filtered through a 0.45 um membrane filter and stored at 4 °C. Nutrient and organic analyses of filtered OGSIR stormwater was conducted at OSU's CCAL facilities. Both inorganic and organic carbon were measured using method APHA 5310B on a Shimadzu TOC-VCSH Combustion Analyzer instrument. Bromide, chloride, and sulfate were measured using method(s) APHA 4110 B; EPA 9056A on a Dionex 1500 Ion Chromatograph instrument. Alkalinity was measured by APHA 2320, titrated to pH 4.5. Modifications: Use 0.02N Na₂CO₃ and 0.02N H₂SO₄ on a ManTech PC-Titrate Auto Titrator System instrument. Nitrite, nitrate, and orthophosphate were measured with method(s) APHA 4500-NH₃ H; EPA 350.1 (salicylate) on a Lachat QuikChem 8500 instrument. Both total nitrogen and total phosphorus are measured with method(s) APHA 4500-NO₃ F; APHA 4500-P J. Persulfate digest, APHA 4500-P B; APHA 4500-P E; EPA 365.2. Persulfate digest on a Technicon Auto-Analyzer II instrument. Lastly magnesium, potassium, and sodium are measured through method APHA 3111 B; flame atomic absorption spectroscopy on a Shimadzu AA-7000 instrument. (Kanalos 2021)

Additional PAH reporting tables:

Table S 1: Parent PAHs in post-LID Inlet.

PAH (pg/mL) ± std. err. of μ	LID Inlet - J0		
	Storm 1	Storm 2	Storm 3
Naphthalene	1.20 ± 0.43	< LOD	< LOD
Acenaphthylene	< LOD	< LOD	< LOD
Acenaphthene	< LOD	< LOD	< LOD
Fluorene	< LOD	< LOD	< LOD
Phenanthrene	1.69 ± 0.28	< LOD	7.37 ± 4.95
Anthracene	< LOD	< LOD	8.47 ± 10.44
Fluoranthene	5.25 ± 0.94	1.75 ± 0.34	1.45 ± 0.83
Pyrene	5.82 ± 1.19	16.29 ± 11.18	1.48 ± 0.86
Retene	4.61 ± 0.76	< LOQ	< LOD
Benz(c)fluorene	0.44 ± 8.43	20.06 ± 8.19	< LOD
Benzo(a)anthracene	< LOD	< LOQ	< LOD
Chrysene+Triphenylene	7.59 ± 1.54	4.15 ± 0.32	3.97 ± 0.80
Benzo(b)fluoranthene	2.99 ± 0.07	2.36 ± 0.39	7.23 ± 5.89
Benzo(k)fluoranthene	1.99 ± 0.28	0.96 ± 0.23	1.96 ± 1.69
Benzo(e)pyrene	3.65 ± 0.16	< LOD	3.97 ± 3.09
Benzo(a)pyrene	< LOD	< LOD	< LOD
Indeno(1,2,3-cd)pyrene	< LOD	12.48 ± 10.19	< LOD
Dibenz(a,h)+(a,c)anthracene	< LOD	14.47 ± 11.82	< LOD

Benzo(ghi)perylene	< LOD	8.99 ± 3.67	< LOD
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Table S 2: Parent PAHs in post-LID Outlet.

PAH (pg/mL) ± std. err. of μ	LID Outlet - J1		
	Storm 1	Storm 2	Storm 3
Naphthalene	< LOD	< LOD	NA
Acenaphthylene	< LOD	< LOD	
Acenaphthene	< LOD	< LOD	
Fluorene	< LOD	< LOD	
Phenanthrene	0.64 ± 0.13	< LOD	
Anthracene	< LOD	< LOD	
Fluoranthene	18.35 ± 7.67	< LOD	
Pyrene	27.22 ± 10.11	1.68 ± 1.97	
Retene	17.36 ± 7.43	< LOD	
Benz(c)fluorene	12.41 ± 9.12	9.91 ± 8.09	
Benzo(a)anthracene	< LOD	< LOD	
Chrysene+Triphenylene	24.09 ± 9.89	1.57 ± 0.85	
Benzo(b)fluoranthene	7.19 ± 2.86	0.94 ± 0.38	
Benzo(k)fluoranthene	6.34 ± 2.60	0.74 ± 0.27	
Benzo(e)pyrene	5.76 ± 2.32	0.77 ± 0.32	
Benzo(a)pyrene	< LOD	< LOD	
Indeno(1,2,3-cd)pyrene	< LOD	< LOD	
Dibenz(a,h)+(a,c)anthracene	< LOD	14.78 ± 12.07	
Benzo(ghi)perylene	< LOD	< LOD	

Table S 3: Parent PAHs in after Biochar treatment.

PAH (pg/mL) ± std. err. of μ	After Biochar - J3		
	Storm 1	Storm 2	Storm 3
Naphthalene	0.32 ± 0.23	< LOD	< LOD
Acenaphthylene	< LOD	< LOD	< LOD
Acenaphthene	< LOD	< LOD	< LOD
Fluorene	< LOD	< LOD	1.57 ± 13.72
Phenanthrene	< LOD	< LOD	3.32 ± 1.75
Anthracene	< LOD	< LOD	< LOD
Fluoranthene	1.70 ± 1.25	< LOD	2.01 ± 3.74
Pyrene	1.65 ± 1.59	< LOD	1.72 ± 2.05
Retene	1.62 ± 1.67	< LOD	1.84 ± 3.93
Benz(c)fluorene	0.64 ± 8.59	< LOD	< LOD

Benzo(a)anthracene	< LOD	< LOD	< LOD
Chrysene+Triphenylene	2.83 ± 2.11	< LOD	4.77 ± 4.02
Benzo(b)fluoranthene	1.07 ± 0.90	< LOD	14.07 ± 1.03
Benzo(k)fluoranthene	< LOD	< LOD	3.92 ± 0.72
Benzo(e)pyrene	< LOD	< LOD	7.08 ± 0.33
Benzo(a)pyrene	< LOD	< LOD	< LOD
Indeno(1,2,3-cd)pyrene	< LOD	< LOD	< LOD
Dibenz(a,h)+(a,c)anthracene	< LOD	< LOD	< LOD
Benzo(ghi)perylene	< LOD	< LOD	< LOD

Table S 4: Parent PAHs in after RemBind treatment.

PAH (pg/mL) ± std. err. of μ	After RemBind - J4		
	Storm 1	Storm 2	Storm 3
Naphthalene	0.91 ± 0.46	< LOD	3.00 ± 5.12
Acenaphthylene	< LOD	< LOD	< LOD
Acenaphthene	< LOD	< LOD	< LOD
Fluorene	< LOD	< LOD	< LOD
Phenanthrene	< LOQ	< LOD	6.98 ± 11.89
Anthracene	< LOD	< LOD	< LOD
Fluoranthene	3.88 ± 3.17	< LOD	0.46 ± 1.20
Pyrene	3.51 ± 2.72	7.26 ± 4.93	0.53 ± 1.54
Retene	3.30 ± 3.05	< LOD	1.61 ± 1.75
Benz(c)fluorene	0.73 ± 8.67	< LOD	< LOD
Benzo(a)anthracene	< LOD	< LOD	< LOD
Chrysene+Triphenylene	4.54 ± 3.91	0.72 ± 1.00	< LOD
Benzo(b)fluoranthene	1.86 ± 1.62	< LOQ	< LOD
Benzo(k)fluoranthene	1.40 ± 1.22	< LOQ	< LOD
Benzo(e)pyrene	< LOD	< LOQ	< LOD
Benzo(a)pyrene	< LOD	< LOD	< LOD
Indeno(1,2,3-cd)pyrene	< LOD	< LOD	< LOD
Dibenz(a,h)+(a,c)anthracene	< LOD	< LOD	< LOD
Benzo(ghi)perylene	< LOD	< LOD	< LOD

Reporting and Dissemination

Peer-reviewed Publications (to date)

Prettyman, K.; Babbar-Sebens, M.; Parrish, C. E.; Babbar-Sebens, J. M. (2020) A Feasibility Study of Uninhabited Aircraft Systems for Rapid and Cost-Effective Plant Stress Monitoring at Green Stormwater Infrastructure Facilities. *Journal of Hydroinformatics*, jh2020195. <http://doi.org/10.2166/hydro.2020.195>.

Wells, J. and Wilson G. (2022) Sediment Deposition Characteristics in Shallow Saturation Excess Overland Flow for Urban Stormwater Applications. *Hydrological Processes*, 36 (8), e14647. <https://doi.org/10.1002/hyp.14647>.

Manuscripts in progress

Parker, B., Kanalos, C., Radniecki, T.S., Simonich, S.M. and Field, J. (in-preparation). "Selection and Optimization of Sorbents for a Treatment Train Approach to Remediation of Heavy Metals and PFAS in Stormwater."

Parker, B.A., and Hilliard, R., Radniecki, T.S., Simonich, S.M. and Field, J. (in-preparation). "Greenhouse-Scale Comparison of 10 Native Pacific Northwest Plants for Maximum Uptake of Per- and Polyfluoroalkyl Substances (PFAS) in Stormwater."

Hilliard, R. and Radniecki, T.S. (in-preparation). "The Evaluation of 10 Native Oregon Plants for the Removal of Heavy Metals and Nutrients from Stormwater - A Greenhouse Study."

Hilliard, R. and Radniecki, T.S. (in-preparation). "The Influence of Bacterial and Fungal Community Structure on the Removal of Per- and Polyfluoroalkyl Substances (PFAS), Heavy Metals and Nutrients from Stormwater in Bioswale Mesocosms."

Rodman, K., Berninghaus, A.E. and Radniecki, T.S. (in-preparation). "The Effect of Naturally Occurring Biofilms on the Removal of Heavy Metals, Nutrients and Organic Carbon from Stormwater by Biochar and Activated Carbon."

Saduaova, A., Hilliard, R., Radniecki, T.S., Babbar-Sebens, M. (in-preparation). "A Field-Scale Evaluation of a Bioswale-Sorbent Low-Impact Development (LID) Hybrid Treatment Train for the Removal of Heavy Metals, Nutrients and Organic Carbon from Stormwater"

Presentations

Babbar-Sebens, M., Prettyman, K., Parrish, C., and Babbar-Sebens, J. "On the use of Uncrewed Aircraft Systems for Monitoring of Plants at Green Stormwater Infrastructure Facilities." *ASCE's World Environmental & Water Resources Congress*, Atlanta, GA, June 5-8, 2022.

Radniecki, T.S., "Redesigning infiltration bioswales to remove dissolved stormwater contaminants" *Oregon Association of Clean Water Agencies – Stormwater Committee*, online, November 10, 2021

Radniecki, T.S., “Redesigning infiltration bioswales to remove dissolved stormwater contaminants” Northwest Environmental Business Council Meeting, online, June 16, 2021

Piemonti, Wilson & Babbar-Sebens; “Challenges and Opportunities in Tracking Sediment-Associated Contaminants in Green Stormwater Infrastructure, oral presentation at American,” *Geophysical Union Fall Meeting*, San Francisco CA & remote, Dec 2020.

Wells, J., Babbar-Sebens, M., Wilson, G., Simonich, S.L., Field, J.A., Piemonte, D., Parker, B. and Radniecki, T.S, “Planning for field-scale bioswale performance evaluation and the OSU OGSIR facility” *Clean Water Initiative Virtual Conference*, online, September 1, 2020

Rodman, K., and Radniecki, T.S. “The effects of biofilms in column testing of adsorbents for the removal of copper, zinc and nutrients from stormwater.” *Clean Water Initiative Virtual Conference*, online, September 1, 2020.

Hilliard, R.F. and Radniecki, T.S. “Investigation of Oregon native plants for remediation of trace metals and organic pollutants in stormwater.” *Pacific Northwest Clean Water Association 2019 Conference*, Portland, Oregon, September 13-16th, 2019.

Student & Trainee Milestones of Participation

High School students: 2

Undergraduate Researchers: 4

Graduate Students:

MS degrees: 3

PhD degrees: 2, 1 in progress

Post-doc Appointments: 1

Faculty Research Assistants: 2

Support of Small Businesses

We have recently installed biochar from Stormwaterbiochar.com and immobilized RemBind from AquaBlok in our field-scale stormwater research facility (*i.e.* OGSIR). Both of these companies are considered small businesses. The data produced from the field-scale testing of these products will be an invaluable resource as a proof of the effectiveness of their products, which they can use to help grow their businesses.

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