Stormwater Treatment Process Quantitative Evaluation

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FINAL DELIVERABLE

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EXECUTIVE SUMMARY

Stormwater runoff serves as a major transport pathway for pollutants into aquatic ecosystems, necessitating the development of effective treatment strategies. Biofiltration, also known as bioretention, is a widely implemented structural best management practice (BMP) for achieving water quality objectives. These systems are often perceived as a “black box” in terms of water quality control. Prescriptive design guidance in many California BMP design manuals provide generic guidance thought to result in treatment to the “maximum extent practicable” without proven links between design instruction and water quality outcomes. The lack of a mechanistic understanding of BMP performance has hindered the development of predictive tools for designing and evaluating biofiltration systems, leading to variable and unpredictable treatment outcomes.

Engineered media in biofiltration BMPs typically includes sand and amendments to achieve water quality objectives. While the effectiveness of these media in removing specific contaminants is often qualitatively tied to the types of media or amendments used, the key to their performance lies in the inherent properties of the media that drive the contaminant removal mechanism. The research conducted herein aims to demystify the BMP “black box” by identifying the measurable physicochemical properties of engineered media responsible for removing representative contaminants from stormwater runoff. A series of laboratory-based experiments, including media characterization, batch-scale tests, and column-scale studies, were conducted to evaluate treatment mechanisms and the performance of media with varying properties. Column studies were used to quantify performance in terms of measured effluent concentrations (i.e., how “clean” is the treated runoff?), deterioration in treatment effectiveness with accumulated pollutant loading, and the total capacity of the media to remove contaminants (i.e., how long does the media last?). These experiments informed the selection and initial development of the model concept and a work plan for integrating laboratory and field monitoring data into a mechanistic, predictive model.

The study focused on the treatment efficacy of engineered media for removing dissolved copper (Cu) and per- and polyfluoroalkyl substances (PFAS). Dissolved Cu was selected as a representative heavy metal that has not been well studied in biofiltration. PFAS, as emerging contaminants, require first-of-its-kind evaluation of their treatment in biofiltration systems. Literature suggests that both contaminants are removed via sorption to media in non-vegetated biofiltration systems. In this study, we deliberately eliminated vegetation and organic matter (e.g. compost) in engineered media mixtures to focus on sorption as the primary removal mechanism.

The laboratory phase aimed to quantify the sorption-based removal mechanisms and establish a scientific basis for developing predictive tools to enhance BMP design and performance. The research began with pilot testing to source and select media, refine methodologies, and narrow scope and experimental parameters. Six engineered media components — including ASTM C33-compliant sand and amendments including regenerated activated carbon (RAC), three biochars, and zeolite — were characterized for their physicochemical properties. Then batch experiments determined sorption isotherms, while column experiments simulated field conditions to assess effluent concentrations over time and treatment capacity for long-term media performance.

Batch tests assessed sorption affinity (K_d) for dissolved Cu, revealing a strong correlation ($r = 0.88$) between cation exchange capacity (CEC) and Cu sorption. This suggests that CEC can serve as a predictive tool for selecting biofiltration materials for dissolved Cu removal. CEC is a readily available analytical procedure performed in soil testing laboratories[i]. Intermittent flow-through column experiments further evaluated Cu sorption in media mixes composed of sand alone or sand with an amendment. Media with mm-scale particle sizes, reflecting regional design guidance, exhibited infiltration rates of 43–150 cm/h under a 15-cm ponding depth. Results from simulated rainfall volumes of 275−495 cm demonstrated that the sorption capacity of engineered media could be estimated using a volumetric sorption affinity (ρK_d), though kinetic limitations were observed due to high infiltration rates. This represents a crucial step in bridging bench-scale findings with field-scale applicability. In practice, design engineers can apply the ρK_d concept to evaluate potential component ratios in engineered media to maximize treatment outcomes based on available materials.

PFAS removal was assessed by testing four engineered media compositions in the same column settings as dissolved Cu against perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) but at influent concentrations of 1000 ng/L each. Among the media compositions tested, all but one (sand mixed with 15% RAC by volume) were either ineffective or only effective during the initial stages of treatment under our experimental conditions. Columns containing sand amended with 15% RAC reduced PFOA and PFOS concentrations to approximately 300 ng/L and 200 ng/L, respectively, after 307 cm of cumulative rainfall. RAC in the top 25% of the media sorbed 1910 ± 97 ng/g of PFOA and 1832 ± 35 ng/g of PFOS, achieving 92% and 82% breakthrough, respectively. Breakthrough curve analysis estimated a media lifespan of 35−59 years under Southern California rainfall conditions, highlighting its potential for long-term PFAS treatment.

The OpenHydroQual model was identified as a promising tool for simulating sorption processes in biofiltration BMPs. A work plan was developed to configure, calibrate, and validate the

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[i] Several standard methods for measuring CEC are found in the literature[1,2]. In this study, CEC as measured as the sum of exchangeable cations was found as the most reliable predictor of sorption affinity, K_d.

mechanistic model based on OpenHydroQual for predicting dissolved Cu removal in biofiltration systems. This model will be further developed in a subsequent project supported by the Southern California Stormwater Monitoring Coalition (SMC).

Overall, the research successfully identified key BMP design features — specifically, media properties of CEC and ρK_d — that practitioners can use to optimize biofiltration for dissolved Cu. Results on PFAS suggested that the effectiveness of media containing RAC is due to its high hydrophobicity, as measured by contact angle, highlighting the need for future research to investigate contact angle to confirm this observation. Laboratory results established a pathway for developing and validating mechanistic models to improve predictive capabilities. By quantifying treatment processes within biofiltration, this research provides a first step for enhancing BMP design guidance, optimizing BMP performance, and informing maintenance and retrofit decisions. The testing methods established produced robust outcomes that can be repeated for additional pollutants. The research findings can be used to strengthen current BMP design guidance, ensuring alignment between target contaminants and their respective treatment mechanisms. Ultimately, this work supports engineers, watershed managers, and regulators in making science-driven decisions that enhance water quality control and regulatory compliance.

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ACRONYMS

ASTM	American Society of Testing Materials
BMP	Best Management Practice
CEC	cation exchange capacity
EMC	event mean concentration
MS4	municipal separate storm sewer system
SMC	Stormwater Monitoring Coalition
SSA_{BET}	BET (Brunauer, Emmett, and Teller) surface area
TMDL	total maximum daily load

INTRODUCTION

Most structural best management practices (BMPs) have been viewed as a “black box” with respect to their impact on water quality control. BMP field performance is typically measured by comparing influent and effluent water quality, without consideration of treatment processes occurring within the BMP to induce pollutant removal. Prescriptive design approaches are the stormwater industry norm, which set expectations to remove pollutants to the “maximum extent practicable” (MEP)[3], rather than to an effluent quality, system efficiency, or other predictable benchmark. The practical assumption of prescriptive design is that if the recommended procedure is followed and/or specifications are met, then the BMP should perform to the MEP.

Few, if any, mechanistic procedures and/or specifications are offered in BMP design manuals in California or elsewhere. Design guidance for water quality features of most BMPs rely on rules of thumb. For example, the engineered media in bioretention systems is thought to be the most functional component of the BMP for water quality treatment. Specifications for engineered media in guidance manuals are often generalized into criteria for sand, agronomic suitability, chemical suitability, and compost stability. However, none of these criteria directly relate to pollutant removal capability. Parameters such as a particle size distribution (PSD) of aggregate components intended to inform infiltration rates, limitations on phosphorus and nitrogen content (among other parameters) which is intended to prevent the BMP from acting as a source of nutrients rather than a sink, and a range of chemical characterizations intended to inform whether the media will support vegetation. Notably in terms of water quality treatment, only the limitations on phosphorus content in minimizing nutrient export have been proven through field or laboratory testing[4]. The PSD guidance is intended to simplify design procedures for ensuring contact time for pollutant removal; however, studies have shown PSD alone does not predictably indicate infiltration rate[5] and no field-based BMP studies have documented an effect of contact time on pollutant removal[ii].

The basic specification for an engineered media blend for bioretention is predominantly sand (often 60-80% by volume in southern California design manuals), and the remainder as an organic material such as compost, or a mixture of topsoil and compost[6,7]. Alternative materials are allowed (often called amendments), as long as individual components and the total mixture meet the prescriptive instruction in the manual. In practice, amendments are often selected according to the type of material that is “known” or thought to promote water quality

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[ii] It is acknowledged that contact time is a well-established design parameter for drinking water and wastewater treatment unit operations, which typically operate at highly controlled, near-steady state conditions, unlike passively operated stormwater BMPs subject to dynamic natural loads.

treatment. Materials such as biochar, zeolite, activated carbon, etc. are increasingly used in BMPs. The properties of each of these materials may vary by source and/or production or manufacturing process, which suggests that the type of material may not be indicative of actual pollutant removal. In this research, we investigate media properties, rather than type, that promote mechanisms of treatment.

Introducing mechanistic-based design procedures for water quality treatment is hypothesized to ensure more consistent and reliable treatment outcomes. Developing mechanistic tools for predicting water quality treatment will enable stormwater managers and engineers to make better informed decisions for watershed management based on quantitative evaluations of BMPs for water quality.

The research initiated in this project aims to tackle these challenges by identifying and quantifying the treatment mechanisms responsible for removing representative contaminants from stormwater runoff within structural BMPs. This will be achieved through the quantitative laboratory-based experiments and the subsequent development of a mechanistic model.

The outcomes will provide information to advance current BMP design guidance, ensuring the alignment of contaminants with their respective treatment mechanisms. This enhancement in BMP design guidance will assist engineers in designing BMPs that best satisfy water quality objectives. It will also enable watershed managers to make informed decisions and instill confidence in regulators in design procedures and predictions for water quality control.

The research presented herein focuses on biofiltration BMPs for the treatment of two representative contaminants including dissolved copper (Cu) and per- and poly-fluoroalkyl substances (PFAS). Cu is among the most frequently detected contaminants in urban runoff, whereas PFAS are likely to be prevalent due to their widespread use. These contaminants are expected to exist in concentrations differing by orders of magnitude in urban runoff, with dissolved Cu typically found in µg/L levels[8,9] and PFAS found in ng/L levels[10–12]. Selecting contaminants that are ubiquitous but of different nature enhances the applicability of the results to other contaminants removed by sorption. Biofiltration was chosen as a model BMP as it is an increasingly common structural BMP in California. More importantly, its flow-through feature and use of engineered media create a unique opportunity to test targeted contaminants. Both contaminants are expected to be removed through sorption to media in non-vegetated biofiltration BMPs[9,13,14].

Project Scope

The project summarized in this report is comprised of three main elements:

- A literature review to identify representative urban runoff contaminants and the most likely treatment mechanisms in engineered media. The literature review directly leads to hypotheses linking engineered media properties to pollutant treatment.
- A series of laboratory-based experiments, including media characterization, batch-scale tests, and column-scale studies to evaluate treatment mechanisms and the performance of media with varying properties.
- Selection and initial development of a model concept and a work plan for integrating laboratory and field monitoring data into a mechanistic, predictive model. This element is also supported by a literature review of the state of the practice in stormwater quality modeling.

Recognizing that biofiltration/bioretention is among the most commonly studied BMPs in the literature, priority was placed on conducting research on less well studied contaminants. In the case of biofiltration, contaminants including zinc, phosphorus, nitrogen, and total suspended solids have commonly been studied in both field and laboratory investigations, and were thus immediately excluded from consideration.

A research focus quickly emerged on dissolved contaminants because dissolved contaminants, particularly heavy metals, are likely to pose greater risk to receiving environments compared to those bound to stormwater particulates.

Finally, since the mechanisms for particulate removal by filtration are well understood, the research also focused on the treatment mechanism of sorption. Improving understanding of sorption processes in BMPs is relevant to design because the process can be predicted and manipulated according to physicochemical media properties.

Organization of this Report

This report condenses the majority of project interim deliverables into a single document. Each of the interim deliverables was reviewed by the project technical lead (at a minimum) and feedback was discussed as necessary by email or in an online meeting with the research team for interim decision-making. Modifications to or, in some cases, exclusions of interim documents for the purposes of this final project deliverable are described in the list below. Interim deliverables included:

Task 22.1: Technical memo defining the BMP attributes and rationale for pollutant selection for testing. This was delivered in the form of presentation to the project technical lead and other staff at the State Water Board. The slide deck is attached as an appendix to this report.

Task 22.2: Draft Work Plan for controlled testing, including literature review. A streamlined version of the literature review is included herein that focuses on the two pollutants for which laboratory testing proceeded. The draft work plan is excluded from this report as final methods are fully documented in Task 22.3.ii.

Task 22.3.i: Revised Work Plan. This interim deliverable is excluded from this report as final methods are fully documented in Task 22.3.ii.

Task 22.3.ii: Technical memo documenting controlled experiment results. Two draft manuscripts were completed as the interim deliverable. These manuscripts were reviewed by the project technical lead and SCCWRP's Commissioner's Technical Advisory Group (CTAG). They are now under review by prominent journals. For this report, all of the details included in the manuscripts as supplemental information are herein woven into the text, so that the State Board has a detailed record in one place of the experiments and outcomes.

Task 22.3.iii: Mechanistic model of treatment processes with model documentation. A written literature review on stormwater water quality models followed by a presentation on the model selected for development using the laboratory data was given to the STORMS unit to satisfy the intent of this deliverable. The literature review is included herein and the slide deck is included as an appendix to this report.

Task 22.4: Work Plan for field validation. The Work Plan under consideration by the Stormwater Monitoring Coalition (of which the State Board is a member agency) is included herein.

Task 22.5: At least three tech transfer activities. Slide decks from tech transfer activities are included as appendices to this report.

LITERATURE REVIEW – STORMWATER POLLUTANTS, POLLUTANT REMOVAL MECHANISMS, AND COLUMN STUDIES ON POLLUTANT REMOVAL

Scope

A review of BMP and stormwater databases and peer-reviewed journal articles was conducted to identify knowledge gaps and focus research efforts on novel opportunities in the otherwise popular field of bioretention research. All information from the databases and peer-reviewed articles is synthesized in this document, while a fully annotated review of the peer-reviewed articles is attached as Appendix A. The literature review is intended to help focus laboratory efforts on the treatment processes and experimental conditions that are most important, in order to prevent duplication of effort, shorten testing time, and prioritize tasks.

Monitoring data from the International Stormwater BMP Database, National Stormwater Quality Database, and the Southern California Stormwater Monitoring Coalition's (SMC's) data portal were reviewed to extract information on the occurrence and abundance of Cu in urban stormwater runoff. Information was not available for PFAS in these databases, therefore technical reports and peer-reviewed journal articles were reviewed.

Peer-reviewed articles investigating BMP contaminant removal processes and contaminant removal processes by media in different water matrices such as wastewater and drinking water were also included for review, with an emphasis on column studies. The literature review is intended to identify (1) the key mechanisms and processes for the removal of targeted contaminants by biofiltration and (2) knowledge gaps in the context of stormwater and biofiltration for each contaminant. A set of hypotheses were formulated based on knowledge gaps, and a workplan for pilot testing was developed.

Copper

Prevalence, physicochemical and toxicological aspects, and notable regulations

Cu is one of the most frequently reported metals in urban runoff studies. Cu is mainly from brake pads, building materials, wood preservatives, paints, and algaecides. According to the National Stormwater Quality Database[15], Cu was detected in the majority of urban runoff: in 3279 out of 3794 samples (86.4%). The total Cu concentration in urban runoff ranged from 0.3 to 1360 µg/L, with a mean concentration of 26.5 µg/L.

The total Cu concentrations in runoff depended highly on land use. The mean concentration from freeways and institutional land use was 43.7 and 10.9 µg/L, respectively, which represent the highest and the lowest mean concentrations among the six types of land use characterized (including residential, commercial, industrial, freeway, institutional, and open space). The SMC stream survey reported a mean total concentration of Cu of 91.0 µg/L, which was more than three times higher than the national mean of 26.5 µg/L. The highest concentration detected was 3200 µg/L, suggesting potentially elevated Cu concentrations in southern California.

Cu in stormwater may occur in particulate, colloidal, or dissolved form[16]. The total dissolved Cu concentration in urban runoff ranged from 0.1 to 195 µg/L, with a mean concentration of 11.3 µg/L. On average, the dissolved Cu concentration was 43% of the total[15]. Based on the SMC stream survey, the mean concentration of dissolved Cu was 59.18 µg/L, with the highest up to 1700 µg/L. The mean Cu concentration was 65% of the total, suggesting that approximately half of the total Cu remains dissolved in urban runoff overall.

Many metals in urban runoff are predominantly associated with particulates, thereby being removed with particulates through physical processes such as sedimentation and filtration. However, since a significant portion of Cu is found in dissolved form, Cu is removed to a lesser degree by removing particulates. Lange et al. (2020) assessed the speciation of metals including Cu in the inflow and outflow of bioretention and found that the percentage of dissolved and colloidal Cu increased significantly in the outflow compared with those in the inflow, suggesting that bioretention preferentially removed particulate Cu over truly dissolved and colloidal Cu[16].

Although site-specific associations may vary, studies have found that a significant portion of dissolved Cu exists in free ionic form, i.e., Cu^{2+}, which is the form closely related to aquatic toxicity due to its higher bioavailability[16,17]. The Maximum Contaminant Level (MCL) for copper in drinking water set by the EPA in the U.S. is 1.3 mg/L. This is to ensure copper concentrations in drinking water remain below a level where potential health risks may occur, particularly for sensitive populations. The California Motor Vehicle Brake Friction Material Law limited Cu content of automobile braking pads to a maximum of 5% by weight by 2021, controlling Cu from entering California waterways.

The current research will study dissolved Cu and free Cu^{2+}, which are known to be most relevant to ecotoxicity yet significantly understudied. Conversely, while Cu may bind to particulates, (1) particulates have been most intensively studied among all types of contaminants in the context of stormwater BMPs; (2) BMPs have been shown relatively effective in removing particulates, (3) Cu bound to particulates are less mobile and bioavailable, thus has less implications for aquatic ecotoxicity. The potential of contaminant leaching, including Cu, from particulates will be beyond the scope of this research.

Treatment processes of Cu in BMPs

The median concentration of total Cu in the outflow of bioretention BMPs was 7.13 µg/L[9], indicating bioretention is relatively effective in removing both total and dissolved Cu[18]. Dissolved metals are removed mainly by sorption and precipitation processes. Sorption, defined as the partition of solutes to solid surface, is identified as the most important removal mechanism for most metals in BMPs[9]. Sorption itself is a general term that encompasses electrostatic interaction, hydrophobic interaction, ion exchange, etc. Sorption can be influenced by factors including pH, dissolved organic carbon, carbonate concentrations, co-constituents competing for adsorption sites, and other factors.

As Cu^{2+} is a positively charged heavy metal species, the pH of the solution is identified as an important parameter influencing the sorption capacity of a material for Cu^{2+}[19,20]. pH affects the solubility, speciation, precipitation of metal ions (including Cu^{2+}), and the surface charge of sorbents. Gupta et al. (1998) assessed Cu sorption to activated slag under pH 2—8[19]. Cu uptake increased with increasing pH and was highest at pH around 5, which was attributed to low zero point of charge of activated slag (pH_{ZPC}= 2.8) and negative zeta potential, i.e., the degree of negative surface charge, at pH>2.8. The pH_{ZPC} of activated sludge was determined by its major components, silica and alumina, pH_{ZPC}s of which were ca. 2.3 and ca. 8.2, respectively. The decrease in Cu uptake at pH above 5 is presumably due to Cu^{2+} complexation with OH^- or other anions in background solution. In addition to pH_{ZPC}, the authors also measured the porosity and surface area of the activated slag, which were 67.5% and 107 m^2/g, respectively. Based on a column study, Gabaldón et al. (2000) reported almost 2 times higher Cu uptake at an influent pH 6.0—6.5 than pH 4.5—5.0[20]. The higher Cu uptake at higher pH demonstrates that Cu^{2+} removal could be more effective at higher pH due to lower negative zeta potential, but also depends on the composition of background solution. While the pH of stormwater runoff has been reported in the range of 6 to 9, the mean value was 7.3[15], providing a desirable pH condition for Cu removal, if the pH_{ZPC} of the media are lower than neutral pH. Other than pH, the role of organic carbon[21], flow rate, initial Cu concentrations[20,22] have been studied for Cu removal, but the results were not conclusive and highly depended on experimental conditions.

Modeling Cu sorption

Efforts have been made to model Cu sorption observed in batch and column experiments. For batch experiments, kinetic analysis on Cu sorption curves confirmed that the rate-limiting step was the diffusion of Cu to the media[19,20]. A series of Cu sorption curves was fitted to isotherm equations, including Langmuir, Freundlich, Temkin, Redlich-Peterson, or Koble-Corrigan[19,20,22]. Sorption isotherms are the relationship between the amount of solute sorbed onto a sorbent and the concentration of the solute at the sorption equilibrium. By fitting batch experiment data to an isotherm, the maximum capacity of a sorbent and the affinity of sorbent to solute (the pollutant) can be obtained.

For column experiments, pollutant loading and outflow concentration data have been analyzed using breakthrough models such as Adams-Bohart, Yoon-Nelson, Thomas models or one-dimensional transport model under steady-state flow conditions where pore-diffusion was assumed as the rate-limiting step[20,22–24]. Through a modeling exercise using multiple breakthrough models, Han et al. (2009) reported that the Thomas model better estimated outflow concentrations over the number of pore volumes than the Adam-Bohart model[22], whereas Al-mahbashi (2022) reported that the Yoon-Nelson model performed better than the Adam-Bohart model and Thomas model[23]. Gabaldón et al. (2000) applied a one-dimensional transport model to the results from their column study and reported that the model predicted the initial zone of the breakthrough curves well but failed to capture the tail zone of the curve[20]. In another study conducted by Spahr et al. (2022)[24], a similar one-dimensional intraparticle diffusion-limited model was successfully applied to estimate the breakthrough curve of the sorption of a trace organic contaminant. These studies evaluated the applicability of different breakthrough models but did not explain or explore why one model is better at estimating outflow concentrations than the others.

Han et al. (2009) suggested a method that uses parameters of the isotherm obtained from the batch experiments to predict the breakthrough curve of a column study using a mass transfer model[22], which can be a way to connect results of batch and column experiments. When breakthrough curves are obtained at different depths of a column or from columns with different depths[19,22], a bed-depth service time (BDST) model can be applied to estimate the breakthrough curve at different depths. BDST model deals with the movement of sorption wavefront through the column, which is useful for determining media exhaustion time for practical purposes such as maintenance or regeneration.

Knowledge gaps and research questions

Literature abounds with column studies focused on a specific medium or media mix and its performance of Cu sorption. However, it is still difficult to predict the performance when inflow water chemistry changes, e.g., pH, pollutant concentration, presence of co-pollutants, mainly due to the lack of thorough material characterization[19,20,22,23]. In studies where different medium types are compared, the conclusion is typically limited to the comparison between specific medium types rather than their common properties[24,25], which makes the performance of a BMP difficult to predict when encountering a different medium. Here we aim to create transferable results, i.e., a process-based model, by delineating the relationship between the common measurable properties of medium and the treatment processes induced by the properties.

Physical sorption of stormwater pollutants by media is a ubiquitous process, which occurs when pollutants in the aqueous phase encounter a solid phase, i.e., a media component. Sorption is particularly important for passive treatment systems, such as BMPs, where pollutants in runoff are expected to be treated by flowing through a media[26]. While sorption happens ubiquitously, there are properties of media that are practically defined to represent the capacity of a media to sorb specific classes of pollutants. Cation exchange capacity (CEC)[21,27] and specific surface area[23–25] are such properties. CEC is defined practically by determining the capacity of a material to retain positively charged ions, i.e., cations, and has been considered a property indicative of the effectiveness of a medium for heavy metal remediation[1,28]. Specific surface area, e.g., BET surface area, refers to the total surface area of a material per unit mass or volume. Specific surface area includes not only the area around the geometry of the material, but also the internal area created by a porous structure, which provides additional sites for sorption to occur[29].

There are also properties of media that are known to trigger specific sorption mechanisms (e.g., electrostatic interaction, hydrophobic interaction). Zeta potential and hydrophobicity are such properties. The zeta potential of a material represents the strength of surface charge at a specific pH. Zeta potential is crucial to the sorption of charged compounds, including a lot of free metals, as it triggers electrostatic interaction[19,25]. Hydrophobicity is the measure of a material to repel or resist its interactions with water, e.g., hydrogen bonding. As materials with higher hydrophobicity preferably sorb other components, including pollutants, on their surface than water, a medium with higher hydrophobicity has shown higher removal for organic pollutants[30,31].

Cu Treatment Hypothesis

We hypothesize that the CEC and/or specific surface area of the medium determine the capacity of cationic (e.g., Cu^{2+}) and organic pollutant sorption. Likewise, the zeta potential and/or hydrophobicity (contact angle) of the medium influence the affinity of cationic and organic pollutant sorption.

These hypotheses are derived from our understanding of common properties of media and their impact on sorption processes from the literature. When the hypothesis is applied to a given storm event for Cu sorption, the Cu concentration in outflow is expected to be determined by the flow rate, total accumulative Cu load, the amount of medium, and the zeta potential and/or hydrophobicity of medium. When it comes to multiple stormwater events, the total amount of Cu retained by the medium is expected to be determined by the concentration of Cu in inflow, the amount of medium, and the CEC and/or specific surface area of the medium.

PFAS

Prevalence, physicochemical aspects, and notable regulations

PFAS are a group of pollutants that are classified as both CECs and persistent organic pollutants. Due to their widespread use, PFAS have been detected ubiquitously in different environments including stormwater runoff, and at higher concentrations near fire training/response sites, landfills, and industrial sites[32].

Xiao, Simcik, and Gulliver (2012) reported that PFAS was detected in 100% of urban stormwater samples[12]. PFOS and PFOA were the most frequently detected and abundant PFAS compounds[33]. Table 1 summarizes the range of PFAS and PFOA concentrations detected in surface runoff in the USA. While the concentrations of PFAS and PFOA differed from event to event and location to location, detected concentrations were mostly lower than 50 ng/L in urban runoff.

Table 1. PFOS and PFOA Concentrations Reported in Urban Runoff

Source	**PFAS Concentration**		**Sampling Summary**	**Notes**
	PFOS	PFOA		
Kim and Kannan (2007)	≤ 14.6 ng/L	≤ 29.3 ng/L	7 samples from 5 locations after 5 snowfall events and 7 samples from 7 locations after a rainfall event in Albany, NY	Not event mean concentrations (EMCs)
Houtz and Sedlack (2012)	2.6-26 ng/L	2.1-16 ng/L	33 urban runoff samples collected from 12 storms and 10 sites around San Francisco Bay, CA	Not EMCs; PFOS and PFOA were predominant among 17 PFAS compounds
Xiao, Simcik, and Gulliver (2012)	≤ 42.5 ng/L	≤ 30.6 ng/L	7 storm events in 4 locations in Minneapolis and St. Paul, MN	Not EMCs; PFAS concentrations in runoff were highly dependent on land use and nearby sources

Some physicochemical attributes of PFAS that may affect their treatment processes are the fluoroalkyl tails (hydrophobic tails), strong carbon-fluorine bonds, and extremely high thermal and chemical stability[34]. PFOA and PFOS have carboxylate and sulfonate polar groups, respectively, which makes them less hydrophobic and present in anionic form at neutral pH. The solubility of PFOA and PFOS are 9500 mg/L and 680 mg/L[35].

Stormwater has been identified as a potential migration pathway of PFAS in urban water bodies along with the wastewater treatment plants[36,37]. While the understanding of long-term risks of PFAS remains uncertain, US EPA established the health advisory levels at 70 ng/L for the combined concentrations of PFOA and PFOS. In March 2023, US EPA proposed national primary drinking water MCLs for six PFAS, including PFOA and PFOS as individual contaminants (4 ng/L each). Notification levels are nonregulatory, health-based advisory levels established for contaminants in drinking water for which MCLs have not been established. The Division of Drinking Water of the California State Water Resources Control Board set the notification levels for PFOA and PFOS at 5.1 ng/L and 6.5 ng/L, respectively, based on recommendations made by the Office of Environmental Health and Hazard Assessment (OEHHA).

Treatment processes of PFAS by BMPs and knowledge gaps

Little is known about PFAS in stormwater[32], let alone its removal through BMPs. Due to the strong carbon-fluorine bonds, PFAS compounds cannot be degraded through physical or biochemical mechanisms of conventional water treatment methods. Granular activated carbon (GAC) and ion-exchange resins are most used methods for removing PFAS from contaminated groundwater, where sorption is the main mechanism[35,40,41].

Pritchard et al. (2023) evaluated six engineered medium mixtures for removing a suite of co-contaminants comprising five metals and trace organic contaminants including PFAS[14]. Under their experimental conditions, nearly all the organic compounds were removed by biochar- and regenerated activated carbon-amended media over the course of three months of continuous flow. The complete removal of organic compounds is presumably due to the fact that the quantity of organic compounds loaded into the columns was relatively low in comparison to the amount of the media[14]. Parker et al. (2023) assessed the effectiveness of four sorbents, including two biochars and two GACs, on metal and PFAS removal from stormwater and observed that a GAC with a net positive charge was most effective in PFAS removal[13]. They also reported that the presence of organic matter decreased PFAS removal efficiencies of the positively charged GAC from 84—95% to 0—45%, potentially due to the sorption of organic matter onto the surface of GAC and thus the decrease of positive charge on GAC surface. This study emphasizes the impact of other pollutants in stormwater on PFAS sorption processes and highlights the importance of the surface charge of medium, which can be characterized by zeta potential, on the sorption of PFAS compounds when they present in anionic forms[13].

PFAS Treatment Hypothesis

As there are few studies on PFAS treatment processes in structural BMPs, and fewer on the effects of medium properties on PFAS sorption, this project is among the first to systematically assess the role of medium properties in removing PFAS in stormwater runoff. We hypothesize that the CEC and/or specific surface area of the medium determine the capacity of cationic (e.g., Cu^{2+}) and organic pollutant (e.g., PFAS) sorption; the zeta potential and/or hydrophobicity (contact angle) of the medium influence the affinity of cationic and organic pollutant (e.g., PFAS) sorption.

LABORATORY EXPERIMENTS AND RESULTS ON DISSOLVED CU

Introduction

As urban stormwater is increasingly recognized as a major source of contaminants entering water bodies[42–46], developing effective treatment strategies has become essential. This is particularly critical in arid and semi-arid regions, where contaminants tend to accumulate on the landscape during prolonged dry periods, and stormwater reuse for groundwater replenishment is gaining attention as a sustainable water resource strategy in response to extended droughts[47–49].

Heavy metals are among the most commonly detected contaminants in urban runoff[45,8,50] and are found in particulate, colloidal, and dissolved forms [16]. While biofiltration (also known as bioretention) — a widely adopted BMP — is effective in removing particulate and colloidal metals through physical filtration[51,9], dissolved metals present a greater challenge due to their mobility[16,21,24]. This is a concern in jurisdictions that are required to comply with a TMDL for metals to protect downstream water quality[52].

Research has identified sorption as the primary mechanism for removing dissolved metals in biofiltration systems[9,45,53]. Engineered media, mostly sand mixed with specialized amendments, has been explored for its potential to enhance sorption.[16,54]. Amendments such as regenerated activated carbon (RAC), biochar, and zeolite have shown promise in treating metals like Cu, Zn, Pb, and Cd in stormwater[22,24,29,50,55–57]. Both RAC and biochar, cost-effective carbonaceous alternatives to GAC, have recently gained attention for their effectiveness in metal removal from water. The efficacy of these carbonaceous sorbents is attributed to their negative surface charge and porous structure.[56,58,59] Zeolite, an aluminosilicate mineral, has also shown potential for enhancing metals removal due to its deficiency in positive surface charge resulting from the isomorphic replacement of Si(IV) with Al(III).[60]

Historically, biofiltration performance has been tied to the type of media or amendments used[24,57], making it difficult to replicate or enhance performance when those materials are unavailable or have inconsistent properties. Sorption is a fundamental unit process that occurs when contaminants in the aqueous phase (e.g., urban runoff) interact with a solid phase (e.g., media surface) through physicochemical sorption mechanisms such as electrostatic interactions, covalent bonding, hydrophobic interactions, and ion exchange[25,61]. The extent of these interactions depends on the characteristics of both phases (runoff and media) as well as the chemical nature of the target contaminants. In the context of stormwater treatment, media properties are the most practical factors that can be tuned to enhance sorption mechanisms.

Despite the proven treatment effectiveness of various types of media, the specific properties that make certain media more effective for metal sorption remain unclear. These limitations underscore the need to focus on identifying the fundamental, measurable properties that drive sorption. Such an approach would expand the range of viable biofiltration media options and enable more adaptable media designs suited to local conditions and needs.

CEC is an operationally-defined media property that quantifies its capacity to exchange cations with its aqueous environment, allowing it to release inherent cations while retaining environmentally relevant cations, including dissolved metals. CEC is typically quantified by the cations released from the media and the surrogate cations (e.g., NH_4^+, Ba^{2+}, Ca^{2+}) sorbed during an extraction process[1,2]. We hypothesize that the CEC of a media is a controlling property in determining its capacity to sorb dissolved cationic metals from stormwater runoff. In fact, CEC has been quantified in several studies assessing media effectiveness for heavy metal sorption[1,21,28,62].

The goal of this study is (1) to identify measurable properties of individual biofiltration media components that can predict their metals sorption capacity, (2) to assess whether the properties of these components can be superimposed to estimate the sorption capacity of engineered media mixes in biofiltration systems, and (3) to develop an approach to adapt common laboratory mass-based media properties into volume-based terms that better align with the design of biofiltration systems in the field. Cu(II) was selected as the model contaminant because it is a common metal found in urban runoff[8,21,53,63]. While the literature extensively addresses Cu removal in stormwater, fewer studies have focused on dissolved Cu, even though it accounts for about half of the total Cu in urban runoff and poses a greater concern than other Cu species due to its aquatic toxicity[8,17,64].

To this end, six engineered media components (sand, three biochars, RAC, and zeolite) were characterized for their physicochemical properties and evaluated for their capacity to sorb dissolved Cu(II) in a static system (i.e., batch experiments). Intermittent flow-through column experiments were then conducted to assess the treatment effectiveness of four engineered media mixes, based on effluent concentrations and treatment capacity. These column experiments were designed to closely mimic runoff treatment in biofiltration, using Cu(II)-loaded runoff equivalent to 275−495 cm of cumulative rainfall. Finally, the results from the media characterization and batch experiments were used to estimate the sorption capacity of engineered media in biofiltration columns for dissolved Cu(II).

Materials and Methods

Media

The six engineered media components included: PA sand (Pacific Aggregates, CA), which meets ASTM C-33 specifications[65–67], and several amendments, specifically clinoptilolite zeolite (KMI Zeolite, NV), RAC (Calgon Carbon, CA), and three wood-derived biochars referenced in the literature[30,68,69], namely Rogue biochar (Oregon Biochar Solutions, OR), Hydrophobic biochar (Biochar Now, CO), and Hydrophilic biochar (modified from Hydrophobic biochar by DASCO, CA). These materials were sourced from bulk suppliers (Table 2). The claim of biochars as hydrophobic or hydrophilic is as per manufacturer-supplied information.

Table 2. Media vendor information

Media	Product and vendor websites
PA sand	Washed concrete https://pacificaggregates.com/products/
Zeolite	Clinoptilolite https://www.kmizeolite.com/technical-data
RAC	RAC-DSR C 8x30 https://www.calgoncarbon.com/products/dsrc/
Rogue biochar	https://www.chardirect.com/
Hydrophobic biochar	https://biocharnow.com/
Hydrophilic biochar	Hydrophobic biochar was used as the source material, modified by DASCO in collaboration with the Dessert Research Institute, NV.
Glass sand	VitroClean glass filter

Media in size fractions suitable for field-scale biofiltration applications were sourced. The particle size distribution of the media was measured (Table 2); the ranges (D10—D90) of PA sand, zeolite, RAC, Rogue biochar, Hydrophobic biochar, and Hydrophilic biochar are 0.33–2.05 mm, 1.33—3.72 mm, 1.08—3.35 mm, 2.12—5.35 mm, 2.22—5.29 mm, and 0.89—2.25 mm, respectively. VitroClean glass sand (Waterline Technologies, CA), with a particle size range of 0.53—0.95 mm, was sourced for runoff pretreatment, as described below.

Media characterization

Physicochemical properties of all seven materials (including glass sand) were characterized, including contact angle, specific surface area (SSA) using the BET method (SSA_{BET}), CEC, pH, loss on ignition (LoI) for organic content, leaching of NO_3^{-}-N and PO_4^{3-}-P, and bulk density (ρ) (Table 3).

Procedures for these measurements are:

Contact angle (°): The ground media was mounted to form a monolayer on double-sided tape affixed to a precleaned glass slide. One drop of deionized water (8 µL) was dispensed onto the ground media surface using a pipette attached to a 27-gauge syringe needle. Five replicate contact angle measurements between the water drop and the media were conducted on each sample within 5 minutes of preparation using a goniometer (First Ten Angstroms, VA). The average contact angle and one standard deviation were then reported.

SSA_{BET} (m^2/g): SSA was measured through N_2 adsorption for each media, analyzed at 77.35 K with a relative pressure up to 0.3 using an Anton Paar NOVATouch 800 (Austria).

CEC_{Ba} (meq/100g): The media was first saturated with a Ba^{2+} solution, followed by four consecutive rinses with deionized water to remove excess Ba^{2+}. The media was then placed in a Ca^{2+} solution to displace the adsorbed Ba^{2+}. The CEC_{Ba} was determined by calculating the difference between the amount of Ca added and the amount remaining in the solution.

CEC_X (meq/100g): The media was saturated with an ammonium (NH_4^+) acetate solution buffered to pH 7.0 to displace exchangeable cations. After displacement, the major cations, including K^+, Na^+, Ca^{2+}, and Mg^{2+}, were quantified using inductively coupled plasma atomic emission spectrometry (ICP-AES). CEC_X was calculated as the sum of equivalent cations (K^+, Na^+, Ca^{2+}, and Mg^{2+}).

pH: One gram of media was equilibrated in 20 mL of deionized water at 100 rpm for 72 h. After equilibrium, the pH of the extracts was measured using an Oakton pH electrode and a pH/Ion 700 Benchtop Meter (Antylia Scientific, IL).

Loss on ignition (LoI, %): The organic matter content of the media was estimated by measuring the gravimetric weight loss during sample ignition in a muffle furnace at 360 °C for 2 h, following initial oven drying at 105°C.

N and P leaching (mg/kg): Extractable NO_3^--N and PO_4^{3-}-P (ortho-phosphate) were determined using spectroscopic methods. Specifically, 4 g of media was extracted with 20 mL of 2 M KCl to assess extractable NO_3^--N, while 1 g of media was extracted with 20 mL of 0.5 M $NaHCO_3$ for extractable PO_4^{3-}-P (also referred to as Olsen P).

Bulk density (g/cm^3): A 250 mL graduated cylinder was filled with oven-dried media (at 55 °C) up to the 200 mL mark, and the media was then compacted with deionized water. The media's dry weight and compacted volume were recorded to calculate the bulk density.

CEC was measured using two commercially available methods: (1) CEC_{Ba}, which involves Ba^{2+} saturation followed by displacement with Ca^{2+}, with quantification based on the Ca^{2+} loss; (2)

CEC_X, which is quantified by the sum of displaceable K^+, Na^+, Ca^{2+}, and Mg^{2+} on the media following NH_4^+ saturation. Measurements for pH and ρ were conducted in-house at the Southern California Coastal Water Research Project (SCCWRP, CA). The contact angle was measured at the Desert Research Institute (NV), SSA_{BET} was determined by Covalent Metrology Services (CA), and the remaining properties were analyzed at the University of California Davis Analytical Laboratory (CA).

Table 3. Physicochemical properties of engineered media components

Media	Contact angle (°)	SSA_{BET} (m^2/g)	CEC_{Ba} (meq/100g)	CEC_X	pH	LoI (% weight)	NO_3^-N (mg/kg)	PO_4^{3-}P (mg/kg)	Bulk density (ρ) (g/cm^3)
Glass sand*		0.02	2.6	0.3	9.12±0.02	<0.05	<0.5	<20	1.43
PA sand	53.6±9.6	1.13	<2.0	2.1	7.94±0.00	0.13	1.5	<20	1.65
Zeolite	62.6±10.3	15.16	7.6	28.3	9.61±0.03	3.8	20.0	<20	0.88
RAC	71.9±9.4	840.50	3.6	5.5	9.10±0.57	1.4	2.2	424	0.55
Rogue biochar	54.6±14.7	546.51	15.0	25.3	9.58±0.04	74.6	0.8	1324	0.12
Hydrophobic biochar	77.4±9.7	237.05	13.7	7.7	7.75±0.07	66.4	2.2	292	0.17
Hydrophilic biochar**	73.4±7.6	443.62	21.0	19.8	5.99±0.10	53.4	20.0	1232	0.16

* Glass sand is the control material used for runoff pretreatment.

** The designation of the biochar as hydrophilic is based on the name provided by the manufacturer.

Background runoff

To supply the large runoff volumes needed for batch and column experiments, simulated stormwater runoff was generated every 1–2 weeks, providing a repeatable, controllable background runoff that mimics wet-weather conditions. The runoff was generated by spraying tap water ("raining") over one of three sections of an access road leading to a business complex parking lot (Figure 1). Each section was approximately 120 m2 and had not received natural or simulated rainfall for at least one week. The runoff was then directed to a curbside collection point and pumped into one or two 200-L drum(s), as illustrated in Figure 2.

Figure 1. Sections of the access road used to create runoff. Each section (a, b, or c) is approximately 120 m^2 and is located between the Southern California Coastal Water Research Project (SCCWRP) building at 33°41'50" N 117°55'17" W, and the parking lot behind the building.

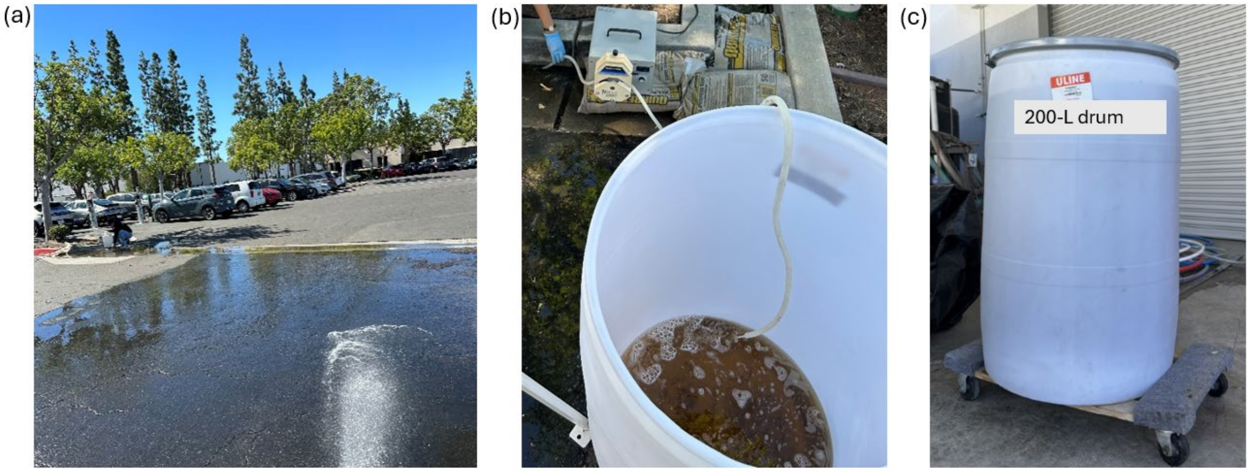

Figure 2. (a) Creating runoff with tap water, (b) pumping runoff into a 200-L drum, (c) runoff collected.

To focus on dissolved Cu, a pretreatment step was performed to remove particulate matter from the runoff. Pretreatment involved filtering the collected runoff through columns filled with 45 cm of VitroClean glass sand at a flow rate of 0.4 L/min (Figure 3a). Without pretreatment, particulates would be filtered out in the surface of the media columns, compromising infiltration rates, interfering with dissolved Cu sorption—the removal mechanism of interest in this study—and complicating data interpretation. In the untreated runoff, the total suspended solids (TSS) ranged from 2—27 mg/L, which aligns with values reported in the literature[8,9]. Pretreatment reduced TSS concentrations below the detection limit of 2 mg/L, demonstrating effective particulate removal from the runoff, without impacting dissolved Cu concentrations. This was confirmed by comparing dissolved Cu concentrations in a runoff sample before and after glass sand filtration, which showed minimal variation (9.36 µg/L and 9.30 µg/L, respectively).

Batch experiments

Batch experiments were conducted to assess dissolved Cu sorption onto media in (pretreated) runoff and to develop isotherms. Duplicate reactors were prepared in 250 mL or 120 mL HDPE bottles, each containing 200 mL or 110 mL of background runoff and initial dissolved Cu ranging from 50 µg/L to 5000 µg/L, with a goal of reaching equilibrium concentrations near that expected in runoff. The two batches of runoff used for the batch experiments contained background dissolved Cu concentrations of 47.5 µg/L and 13.8 µg/L. A 200 mg/L Cu(II) stock solution, prepared from $CuSO_4 \cdot 5H_2O$ (98—102% purity, LabChem, PA), was used to achieve target initial Cu concentrations.

Sorption experiments were initiated by adding individual materials to each bottle in predetermined amounts: 0.5 g for sand and 0.05 g for other media. Initial pH was measured before and after media addition, with adjustments made to reach 7.2 (the pH of pretreated runoff) if outside the range of 7.0─8.5, using concentrated HCl and NaOH (Fisher Scientific, NH). pH-adjusted bottles were placed on an orbital shaker at 120 rpm for 72 h to allow sufficient time for Cu diffusion into pores and equilibration, particularly for RAC and biochars[20,70]. The pH was checked again at 24 h and 72 h, just before sampling. Upon completion, 15 mL samples were collected, filtered through a 0.22 µm hydrophilic nylon filter, and stored in 15 mL polypropylene vials at 4 °C for subsequent analysis.

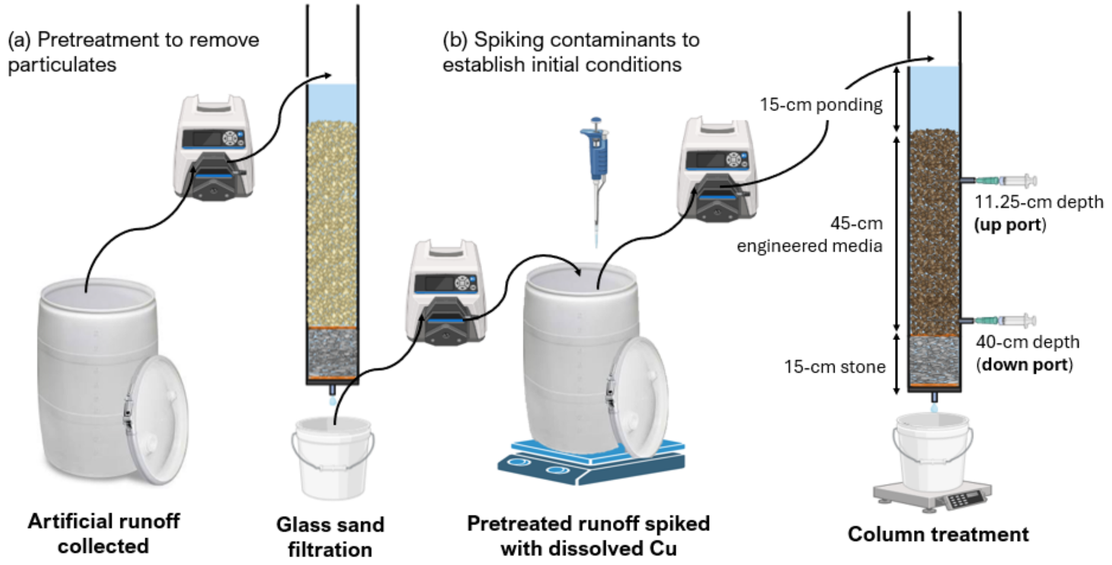

Figure 3. (a) Simulated runoff pretreatment to remove particulates; (b) Spiking contaminants into the pretreated runoff to establish initial conditions for column experiments.

Column construction

The columns were constructed from transparent polyvinyl chloride (PVC), measuring 90 cm in length and 10 cm in diameter. The column structure and media packing processes were designed to closely mimic installation[7,71,72] and 1-dimensional flow in biofiltration BMPs. From bottom to top (Figure 3b), the columns contained a 10 cm layer of washed stone with sizes ranging from 2.5 to 3.8 cm, followed by a 5 cm layer of washed stone with sizes ranging from 1.2 to 2.4 cm. These layers allowed free drainage while preventing media washout. Above this drainage layer, 45 cm of engineered media (typical of a field biofiltration facility in Southern California) were packed into the columns. Media components were mixed for 30 min using a clean Ryobi concrete mixer (model RMX001, Japan) to create homogeneous 4 L batches of media, according to the volume percentages specified in Table 4. The mixed media was placed in the columns using a wet packing method in 15 cm increments, as in field installations, with each layer ponded with 15 cm of tap water to aid compaction, and then allowed to drain before adding the next increment. To prevent media disturbance during stormwater application, the media layer was topped with a layer of washed stone (1.2 to 2.4 cm). Two sampling ports were installed at engineered media depths of 11.25 cm (25% depth) and 40 cm (89% depth). At the base of each column, a shower drain, funnel, and ball valve were installed to allow drainage control if needed. Each component of the drainage system at the base of the columns was tested individually to ensure it did not impede free drainage.

Wooden frames were built to hold a total of 8 columns (Figure 4a). The influent was directed from the supply tank to each column at a constant rate using a multi-channel peristaltic pump, with individual control provided by valves on the supply tube of each column. To manage overflow, an outlet was created by cutting a hole 15 cm above the media surface, allowing a constant ponding depth and redirecting any overflow back to the supply tank. The columns were housed in a temperature-controlled room set to 17.5°C to simulate wet weather conditions in Southern California. When stormwater was not being applied, the entire frame was covered with a black plastic curtain to block light (Figure 4b), replicating underground conditions typical of biofiltration.

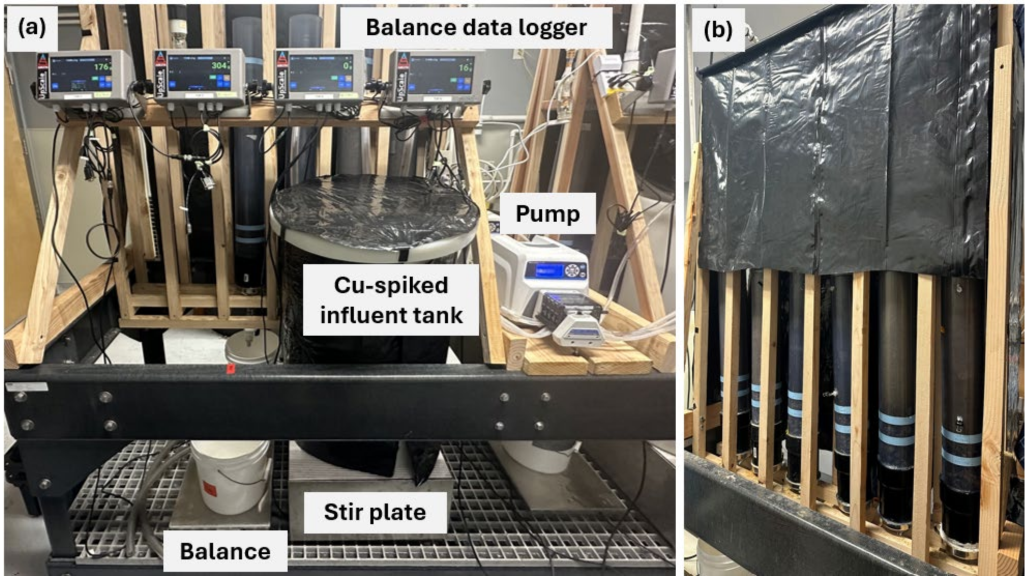

Figure 4. (a) Physical column setup; (b) Column features such as frames and plastic curtain.

Table 4. Summary of column compositions and experimental conditions

Column name	Media composition (by volume)	Amendment mass (%)	Porosity[*] (%)	Infiltration rate (cm/h)	Daily loading rate[**] (cm/d)	Elapsed testing days (d)	Cumulative loading (L)	Cumulative rainfall depth[***] (cm)
PA sand	PA sand only	–	29	58−150	160−400	37	753−877	464−541
10% Rogue	10% Rogue + 90% PA sand	0.8	29	51−112	160−340	37	631−735	389−453
10% Zeolite	10% Zeolite + 90% PA sand	5.6	25	56−183	240−380	24	536−588	330−363
15% RAC	15% RAC + 85% PA sand	5.6	27	43−150	120−320	24	485−515	299−317

[*] Porosity was measured by wet packing a 250 mL graduate cylinder based on the media composition.

[**] The daily runoff depth applied to the columns.

[***] Assuming the cross-sectional area of the column represented 5% of the impervious drainage area.

Column experiments

The columns were initially conditioned with tap water to fully saturate the media and stabilize their infiltration rates. This process involved passing 70—350 L of tap water through each column under a constant ponding depth of 15 cm[73]. Following this conditioning phase, experiments were conducted 2—4 d a week, from February to March 2024 for the first phase, and from June to July 2024 for the second phase (Table 7).

Two column compositions were tested in the first phase: PA sand only and PA sand mixed with 10% (v/v) Rogue biochar, labeled "10% Rogue". Two additional media mixes were introduced in the second phase: PA sand mixed with 10% Zeolite, labeled "10% Zeolite", and PA sand with 15% RAC, labeled "15% RAC". This resulted in a total of 8 columns, with 4 different media compositions, each tested in duplicate. Relatively low amendment ratios (10% v/v for Rogue biochar or zeolite, and 15% v/v for RAC) were selected to achieve media exhaustion within a reasonable experimental timeframe. For both testing phases, the target Cu concentrations in the pretreated runoff were 50 µg/L, which was achieved by spiking Cu stock solutions into the pretreated runoff (Figure 3b). PFOA, PFOS, and NO_3^- were also spiked as co-contaminants using corresponding stock solutions. As summarized in Table 5, during the first phase, the target concentrations for PFOA, PFOS and NO_3^--N were 25 ng/L, 25 ng/L, and 1 mg/L, respectively. In the second phase, the concentrations for PFOA and PFOS were increased to 1000 ng/L, while NO_3^- -N remained at 1 mg/L. Stock solutions were prepared using solid PFOA, 10 mg/mL PFOS in ethanol (both ≥95%, Cayman Chemical, MI), 5 M $NaNO_3$ solution (Cole-Parmer, IL), and a 1000 mg/L Cu standard solution in 1 M KNO_3.

On a column testing day, pretreated runoff was transferred into two 120-L tanks (100 L per tank) and spiked with stock solutions to achieve the target influent concentrations. The spiked runoff in each tank was placed on stir plates at 100 rpm for 15 min prior to the start of experiment to ensure homogenization. Each 100-L spiked runoff served as the supply for 4 columns on that day. Once a constant ponding depth of 15 cm was established (typically taking 3-6 min), the columns were operated in continuous downflow mode for 1.5—3.5 h until the influent tank was exhausted. At the end of each experimental day, the columns were fully drained.

Similar to field biofiltration installations, the media mixture and ponding depth in the laboratory columns were used to regulate flow through the systems. Daily infiltration rates (Table 4) were determined from the slope of effluent stormwater mass over time, starting from the establishment of the 15 cm ponding depth until just before the columns were drained. Effluent mass from each column was monitored in a bucket set atop a data-logging balance (Model 620T-UP-FLOW-DLOG, 25lb capacity, Arlyn, CA). Infiltration rates and sampling times were combined to track the exact amount of runoff depth processed by the columns. A supplemental experiment was conducted where the infiltration rate through the 10% Zeolite columns was manually reduced from 183 cm/h to 73 cm/h using an outlet control.

Table 5. Target contaminant concentrations in the influent in column experiments

Column name	First phase				Second phase			
	Cu (µg/L)	PFOA and PFOS[*] (ng/L)	NO_3^--N (mg/L)	Elapsed testing days	Cu (µg/L)	PFOA and PFOS (ng/L)	NO_3^--N (mg/L)	Elapsed testing days
PA sand	50	25	1	16	50	1000	1	21
10% Rogue	50	25	1	16	50	1000	1	21
10% Zeolite	—	—	—	—	50	1000	1	24
15% RAC	—	—	—	—	50	1000	1	24

[*] PFOA and PFOS, each at the specified concentrations

Sample collection and analysis

Aqueous samples were collected daily from the influent tank and from the two sampling ports (“up” and “down”) of each column (Figure 3b). A 30 mL sample was extracted from the horizontal center of the column using a 5-cm, 16-gauge needle connected to a 50 mL syringe. The samples were filtered through a 0.22-µm nylon filter and stored in a 50 mL polypropylene tube at 4 °C until analysis. The effluent pH was measured at the end of each experimental day using a double-junction pH meter (Antylia Scientific, IL). Selected samples were analyzed for dissolved Cu using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) following EPA 200.8 method by Physis Environmental Laboratories, Inc. (CA) which has a Cu reporting limit of 0.022 µg/L.

Data analysis

Linear regression, along with its slope and confidence intervals, was performed for the isotherms and to evaluate the predictive capacity of media properties using the *lm* function in R. Additionally, Pearson correlation analysis was conducted using the *cor* function in R. Values of the Pearson correlation coefficient (*r*) range from -1 to 1, with values closer to -1 or 1 indicating stronger linear correlations, and values near 0 indicating a weaker linear relationship.

Results and Discussion

Properties of engineered media components

The characterization of the media aimed to assess the sorption-related properties of each media component and gather essential data for evaluating their suitability for biofiltration applications. Sorption-related media properties can be categorized into two groups: (1) properties that evaluate the media's ability to trigger specific sorption mechanisms, such as pH[19,63] and contact angle[31,74], which serve as indicators of electrostatic and hydrophobic interactions, respectively; and (2) properties that assess the media's total capacity to sorb contaminants, such as SSA and CEC[19,22], which typically utilize surrogate sorbates for quantification.

PA sand, an ASTM C33-compliant sand used in biofiltration, was slightly alkaline (pH 7.94) and exhibited the lowest values for contact angle, SSABET, and CEC compared to the amendments. This suggests that limited Cu sorption is expected to occur on the PA sand. The LoI, NO3−-N, and PO43−-P of PA sand were also the lowest of the evaluated media. In contrast to PA sand, the other amendments evaluated spanned a wide range of values for each property. Amendment pH covered and exceeded the pH range (6−8.5) recommended in local BSM design guidance[7,71]. SSABET values also differed substantially, from 15.16 m2/g for zeolite to several hundred m2/g for carbonaceous amendments. These high values are attributed to the internal pore structures formed through pyrolysis and activation processes[24,25,29]. For biochars, despite both Hydrophilic and Hydrophobic chars being derived from the same wood biomass, Hydrophilic biochar exhibited approximately twice the SSABET, CECBa, and CECX of Hydrophobic biochar, confirming that biochar properties can vary depending on not only the source biomass but also production processes[75,76]. Overall, these notable variations in properties allow testing of the hypothesis that CEC, among other properties, may determine the media's capacity to sorb dissolved Cu.

CEC as a predictor of Cu sorption in batch stormwater systems

Sorption isotherms illustrate the partitioning of dissolved Cu between the sorbent phase (engineered media components, C_s) and the solute phase (pretreated runoff, C_{aq_eq}) at sorption equilibrium, as presented in Figure 5. The data from these experiments exhibited a strong positive correlation for all materials, with *r* exceeding 0.95, except for glass sand. The sorption affinity (K_d) of each media component was derived from the slope of the linear isotherm, based on Eq. 1:

$$K_d(L/g) = \frac{C_s}{} \qquad \text{[Eq. 1]}$$

where C_s is the mass of Cu sorbed by each material (µg/g) and C_{aq_eq} is the equilibrium aqueous Cu concentration in its dissolved form (µg/L).

A higher K_d value indicates greater sorption of dissolved Cu to the media at a given equilibrium concentration. As expected, glass sand (used for stormwater pretreatment) showed a K_d of -0.019 with an *r* value of -0.85, indicating negligible sorption of Cu. Among the engineered media components, PA sand exhibited the lowest K_d value (0.259 L/g), which was an order of magnitude lower than the values for the amendments tested.

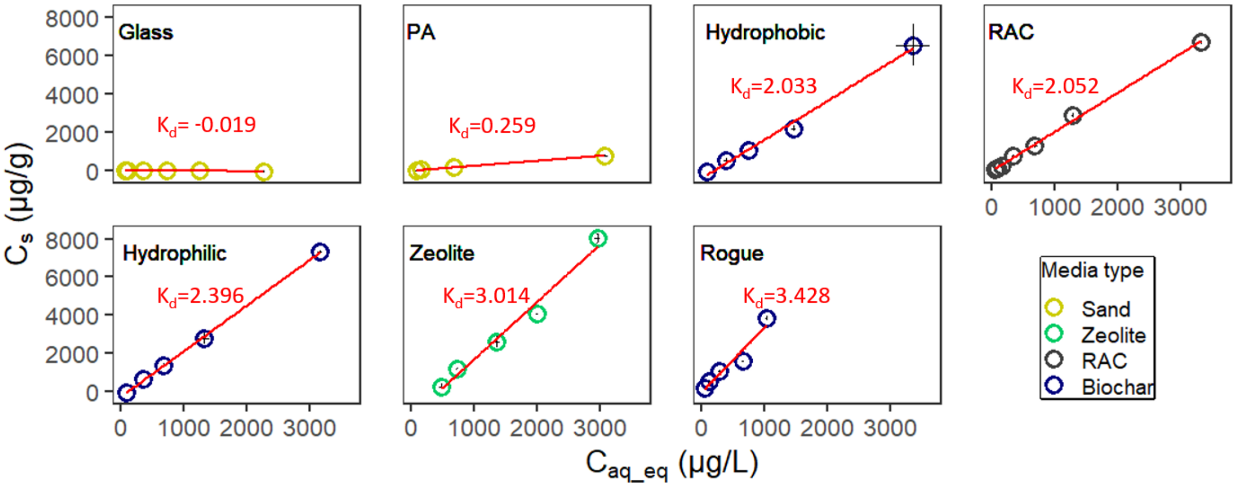

Figure 5. Sorption isotherms of individual materials for dissolved Cu from batch experiments conducted in pretreated runoff (pH 7.0−8.5, TSS<2 mg/L). Mean values from duplicate reactors are plotted. Panels are arranged in ascending order of the slope, i.e., K_d (L/g).

One objective of the batch experiments was to evaluate the sorption-related properties from material characterization as predictors of dissolved Cu sorption. CEC_{Ba} and CEC_X showed the highest correlations to K_d (*r* = 0.65 and 0.88, respectively) among the parameters evaluated (Figure 6), and thus the greatest potential to predict K_d. Therefore, data support the hypothesis that CEC_X is a promising parameter for predicting Cu sorption in batch settings (Figure 7). This correlation is particularly meaningful because it was derived from experiments that included several media types (sand, biochar, RAC, and zeolite) and were conducted in the pretreated runoff, which closely mimics a natural urban stormwater matrix.

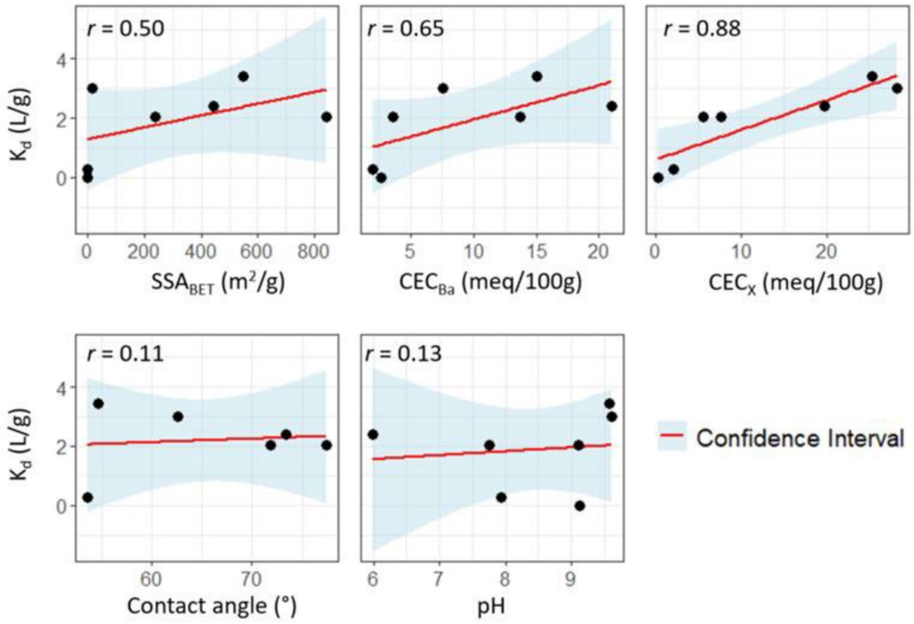

Figure 6. Linear correlation between sorption-related properties from material characterization and K_d obtained from batch experiments. The Pearson correlation coefficient (r) and the confidence interval for each correlation are shown on each panel.

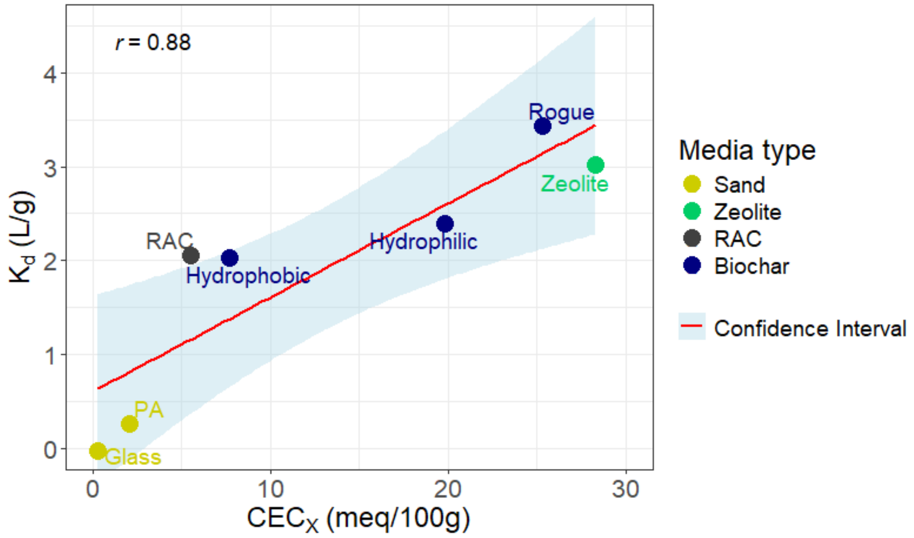

Figure 7. Linear correlation between CECX from material characterization and K_d obtained from batch sorption experiments. Confidence intervals for the slope estimate the range within which the true slope value is likely to fall, with 95% confidence.

BMP design guidance commonly includes CEC in the basic characterization of BSM[7,71]. The inclusion of CEC as a BSM design parameter appears not intended to address contaminant sorption, but due to its implications to retain macronutrients (K^+, Ca^{2+}, Mg^{2+}) essential for plant growth[2,77]. Additionally, BMP design guidance does not specify a standardized method for measuring CEC. The interlaboratory comparison between CEC_{Ba} and CEC_X in this study (Figure 8) revealed notable discrepancies, particularly for zeolite and Rogue biochar, where CEC_X values were higher than CEC_{Ba}. Further analysis of the cation contributions to CEC_X (Table 6) indicates that the high CEC_X for zeolite may be attributed to K^+ at 19.22 meq/100g, and for Rogue biochar, Na^+ at 10.24 meq/100g and K^+ at 7.46 meq/100g. These monovalent cations may not be fully replaced by divalent Ba^{2+} during CEC_{Ba} measurement, leading to lower values. A literature search identified at least five different methods used for measuring CEC[1,2], and found many studies lack detailed descriptions of the methodology used. This study shows the importance of specifying the method used to measure CEC in the context of sorption potential, and that CEC_x is a valuable predictor of Cu sorption.

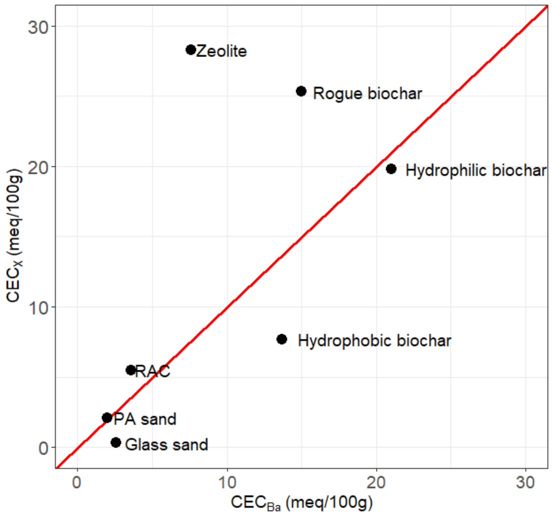

Figure 8. Comparison of CEC_{Ba} and CEC_X

Table 6. Contribution of individual cations (K^+, Na^+, Ca^{2+}, Mg^{2+}) to CEC_X in meq/100 g.

Media	CEC_X[*]	K^+	Na^+	Ca^{2+}	Mg^{2+}
Glass sand	0.3	0.01	0.17	0.12	0.02
PA sand	2.1	0.05	0.13	1.62	0.28
Zeolite	28.3	19.22	<0.004	8.42	0.67
RAC	5.5	0.48	4.00	0.29	2.2
Rogue biochar	25.3	7.46	10.24	1.89	0.8
Hydrophobic biochar	7.7	0.04	4.38	1.26	2.2
Hydrophilic biochar	19.8	0.31	11.29	4.02	20

[*] $CEC_X = K^+ + Na^+ + Ca^{2+} + Mg^{2+}$ with units all in meq/100 g

Dissolved Cu sorption in column experiments

Breakthrough curves for the flow-through column experiments were obtained for four media mixes (varied in K_d and CEC_X values) at two column depths (Figure 9). The columns received Cu-loaded runoff with an average dissolved Cu concentration of 49±5 µg/L. The influent concentrations (Cu_{inf}) fluctuated daily between 40—60 µg/L, due to background Cu concentrations in the collected runoff before spiking. Each column processed different amounts of runoff daily, as indicated by the loading rates (Table 4), because system hydraulics were controlled by the media. This was an intentional experimental design approach to mimic field installations. Over the course of the experiment, the PA sand and 10% Rogue columns received the equivalent of 9—20 years of rainfall, while the 10% Zeolite and 15% RAC received the equivalent of 7—13 years of rainfall, based on an average annual rainfall of 25—38 cm/year in Southern California[78].

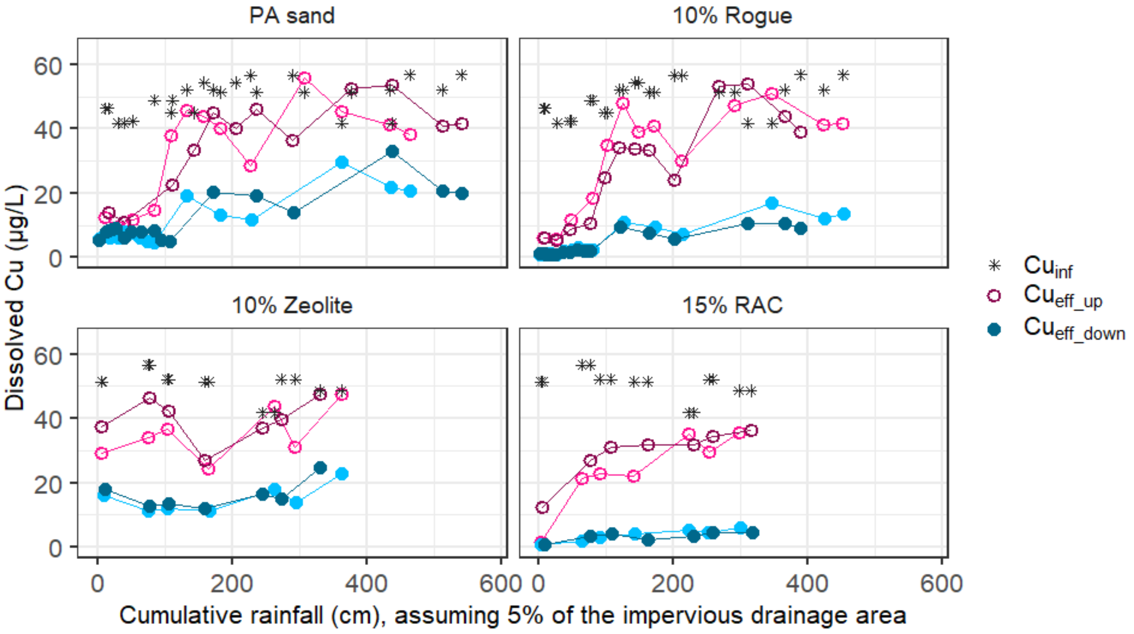

Figure 9. Breakthrough curves for dissolved Cu at the "up" and "down" effluent sampling ports of the biofiltration columns. Influent samples were collected directly from the tanks supplying all columns and applied to all panels, while effluent samples were taken from each port and column. Dark and light-colored symbols represent results from duplicate columns. The pH of all effluent samples ranged from 7.19 to 8.20.

Effluent concentrations. Cu concentrations from the "down" port (Cu_{eff_down}) were measured to assess effluent concentrations after full column treatment throughout the experiment, while Cu_{eff_up} were measured to evaluate the sorption capacity based on media exhaustion. Over the course of the runoff loading, both Cu_{eff_down} and Cu_{eff_up} exhibited an increasing trend. The last measured Cu_{eff_down} ($Cu_{eff\_down\_end}$) in all columns was <50% of Cu_{inf} (Figure 10), indicating continued active removal of dissolved Cu in the full 45 cm of the media. In contrast, Cu_{eff_up} gradually increased to >70% of Cu_{inf}, suggesting that the engineered media at the upper 25% (11.25 cm) were approaching exhaustion.

The first measured Cu_{eff} at each port (Calculated based on measured influent and effluent Cu concentrations using Eq. 2., $Cu_{eff\_down\_0}$ and $Cu_{eff\_up\_0}$) are used to evaluate whether Cu sorption in the columns is kinetically/transport limited and if the sorption efficiency varies with media composition. $Cu_{eff\_down\_0}$ and $Cu_{eff\_up\_0}$ are compared with hydraulic residence times, calculated from the infiltration rates and porosity for each column (Table 4 and Figure 10). For the 10% Rogue and 15% RAC columns, initial low $Cu_{eff\_down\_0}$ (<1 µg/L) concentrations are associated with 4.3—15.0 min residence times in the 40-cm layer; $Cu_{eff\_up\_0}$ of 6-7 µg/L are associated with residence times of 1.2—4.3 min within the first 11.25 cm. This implies that 4.3—15.0 min is required for the complete sorption of dissolved Cu to these media and demonstrates the kinetic limitation of a shallow-depth/rapid infiltration BSM. Kinetic limitations are apparent even at the 40 cm depth ("down" port) for the PA sand and 10% Zeolite columns, as indicated by $Cu_{eff\_down\_0}$ values of 5.4±0.3 and 17.1±0.9 μg/L, respectively. These concentrations are associated with residence times of 4.6—11.9 min for PA sand columns and 3.3—10.7 min for 10% Zeolite columns, suggesting that these times are inadequate for transport and equilibrium sorption to these media. These results demonstrate that the rate of Cu sorption varied with media composition, with sorption to zeolite being the slowest, thereby limiting the utilization of the full Cu sorption capacity of these media.[79,80]

Kinetic limitation in column systems is a key distinction from batch experiments, along with dynamic experimental conditions such as fluctuating influent concentrations and infiltration rates. In batch experiments, an extended time (e.g., 72 hours in this study) is allowed for sorption equilibration, whereas column experiments provide a limited time for sorption to occur, especially when using a coarse media. If the sorption process is slower than or comparable to the residence time, the sorption capacity of the columns is not only constrained by the media's capacity but also by the rate of sorption to the media.

Sorption capacity. The mass of Cu sorbed to the column media over cumulative rainfall was calculated based on the breakthrough curves for the 25% and 89% media depths using Eq. 2.

$$\text{Measured } Cu \qquad (\mathrm{mg}) = \sum (\qquad \frac{\mathrm{mg}}{\mu\mathrm{g}} \qquad \text{[Eq. 2]}$$

where C_{infi} (μg/L) are the measured influent concentrations, and C_{effi} (μg/L) are the measured effluent concentrations from "up" or "down" at the ith sampling event of each column, and v_i (L) is the volume of runoff processed by the column between the (i-1) and ith sampling events. Mean values of Cu_{sorbed} were calculated from duplicate columns, with the range between duplicates representing the variability.

The results showed that the 10% Zeolite columns sorbed the least amount of dissolved Cu, the other three column types sorbed similar amounts, and the 15% GAC columns sorbed slightly more (calculated based on measured influent and effluent Cu concentrations using Eq. 2., Figure 9). The K_d values of the four media components used in the column experiments followed the order of PA sand<RAC<zeolite<Rogue biochar, with PA sand having a K_d an order of magnitude lower than other amendments. However, the ρK_{dj} values followed the order of Rogue biochar≈PA sand< RAC<zeolite (Table 8). The differences in estimated sorption capacity between PA sand and the amendments decrease when considering ρ. PA sand's higher ρ compensates for its lower K_d; an order of magnitude higher ρ of PA sand compared to Rogue biochar results in identical ρK_{d-mm} values for PA sand and the mixed media containing 10% Rogue. Likewise, in the other mixtures, PA sand made up more than 85% (v/v) of the engineered media and is expected to contribute 60% or more of the sorption capacity.

Table 7. Summary of measured experimental results and total Cu sorbed to columns

Column name	Cumulative rainfall (cm)	Up port (11.25 cm depth)			Down port (40 cm depth)		
		$C_{eff\_up\_0}$ (µg/L)	$C_{eff\_\_up\_end}$ (µg/L)	Cu_{sorbed}* (mg)	$C_{eff\_down\_0}$ (µg/L)	$C_{eff\_\_down\_end}$ (µg/L)	Cu_{sorbed}* (mg)
PA sand	502±38	13.2±0.9	40.1±1.7	9±0.5	5.4±0.3	20.4±0.4	23±1.0
10% Rogue	421±32	6.1±0.0	40.3±1.4	9±0.2	0.9±0.2	12.1±1.5	26±1.0
10% Zeolite	346±16	33.3±4.2	47.5±0.1	6±0.8	17.1±0.9	23.9±0.9	19±0.9
15% RAC	306±9	6.9±5.5	35.9±0.5	10±0.4	0.8±0.2	5.3±0.7	23±1.0

* Calculated based on measured influent and effluent Cu concentrations using Eq. 2.

Table 8. Predicted dissolved Cu sorption in columns based on the properties of media components

Column name	PA sand (component 1)				Amendment (component 2)				ρK_{d-mm} (L/cm^3)	Contribution of PA sand*	Cu_{sorbed}** (mg)
	ρ_1 (g/cm^3)	K_{d1} (L/g)	$\rho_1 K_{d1}$ (L/cm^3)	ε_1 (%)	ρ_2 (g/cm^3)	K_{d2} (L/g)	$\rho_2 K_{d2}$ (L/cm^3)	ε_2 (%)			
PA sand	1.65	0.259	0.426	100%	-	-	-	-	0.426	100%	16.7
10% Rogue	1.65	0.259	0.426	90%	0.12	3.43	0.408	10%	0.425	90%	16.6
10% Zeolite	1.65	0.259	0.426	90%	0.88	3.01	2.66	10%	0.650	59%	27.4
15% RAC	1.65	0.259	0.426	85%	0.55	2.05	1.12	15%	0.531	68%	19.8

* Estimated contribution of PA sand to total sorption by engineered media.

** Predicted Cu_{sorbed} by engineered media properties in the first 11.25 cm using Eq. 4.

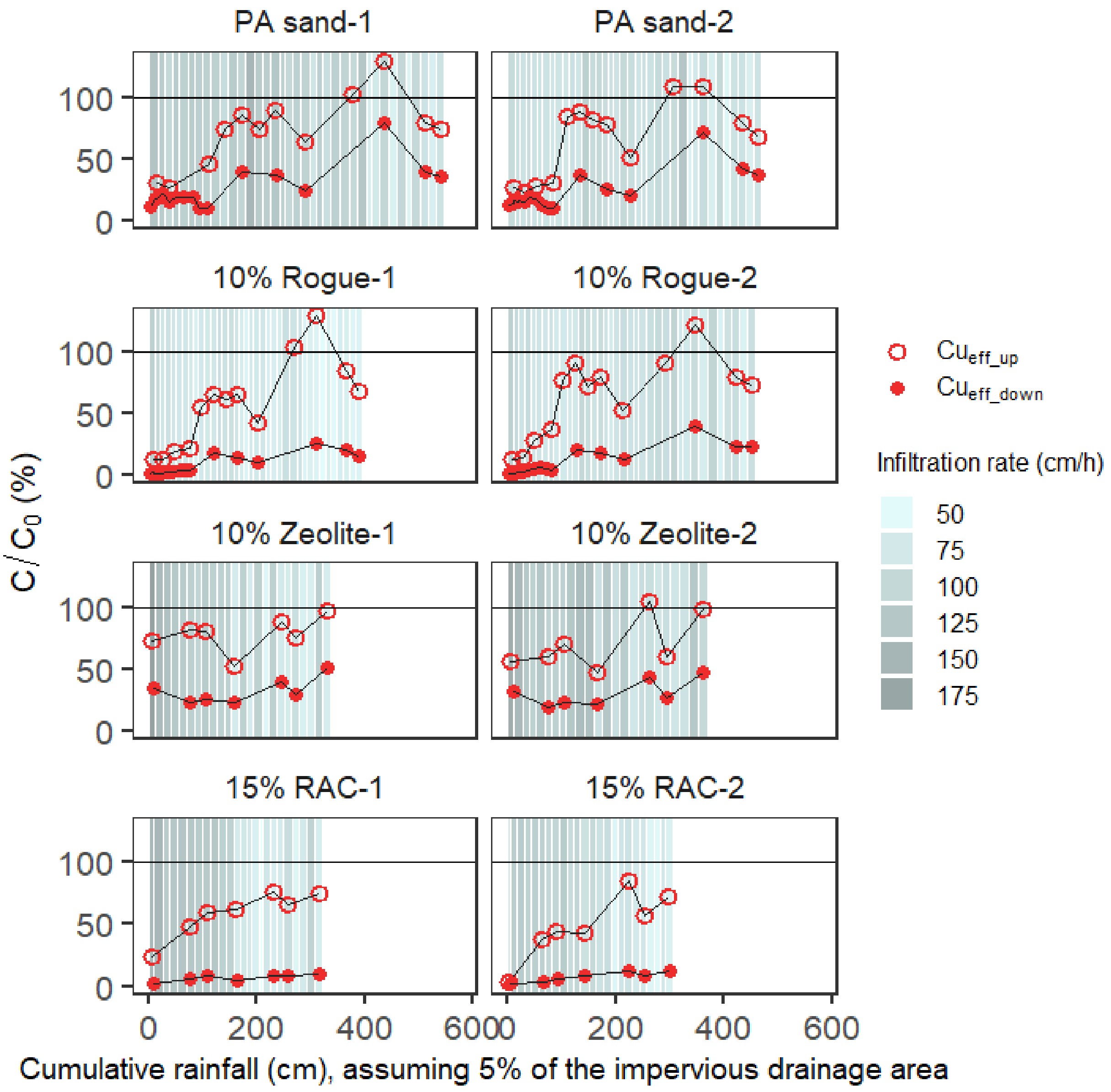

Figure 10. Breakthrough curves showing the percentage of dissolved Cu concentrations at the "up" and "down" effluent sampling ports, relative to their corresponding influent concentrations (C/C_0, %), plotted on the y-axis. Duplicate columns are plotted separately on the left and right panels, respectively, to highlight differences in daily infiltration rates in each column, which are represented by background rectangles filled with varying color shades.

A desktop approach was developed to estimate the sorption capacity of mixed media. K_d (Eq. 1) is expressed per unit mass, but biofiltration systems are typically designed based on BSM volume. Since the media evaluated in this study have a bulk density that varies by a factor of 14, a volumetric K_d was obtained by introducing the media bulk density (ρ). The volumetric K_d

for a unique material *j* is given by $\rho_j K_{dj}$, while the volumetric $K_{d\text{-}mm}$ for a mixed media is estimated from a weighted average of the capacity of each material (Eq. 3):

$$\rho K_{d-mm}(L/cm^3) = \sum_j \rho_j K_{dj} \varepsilon_j \qquad \text{[Eq. 3]}$$

Where $\rho K_{d\text{-}mm}$ is the sorption affinity per unit volume of a mixed media, j denotes the index for a media component, ρ is the bulk density (g/cm^3), ε is the volume fraction of the component in the engineered media.

The mass of Cu sorbed by a specific volume of media was predicted from $\rho K_{d\text{-}mm}$, the average of the last measured influent ($C_{\inf\_end}$) and effluent (C_{eff_end}) Cu concentrations, and the media volume (V_{media}) as described in Eq. 4:

$$\text{Predicted Cu}_{\text{sorbed}}\text{ (mg)} = \rho K_{d-mm} \times \frac{(C_{\inf\_end} + C_{\mathrm{eff}\_end})}{2} \times V_{media} \times 0.001\,\frac{\mathrm{mg}}{\mu\mathrm{g}} \qquad \text{[Eq. 4]}$$

Since the engineered media at the "down" port was far from exhaustion (Table 7), sorption capacity was predicted only for the top 11.25 cm of media (V_{media} = 884 cm^3), assuming no kinetic limitations. C_{inf_end} and C_{eff_end} are equal if/where the sorption capacity of the media above the sampling port is exhausted; in other words the media sorption capacity can be estimated by C_{inf} based on Eq. 1. Since the media above the "up" port did not reach exhaustion, Eq. 4 is used.

The calculation revealed predicted Cu sorption capacities of 16.6−16.7 mg for PA sand and 10% Rogue biochar, and 19.8 mg for 15% RAC (Table 8). The similarities in sorption capacity between PA sand and 10% Rogue biochar, and a higher value for 15% RAC are consistent with experimental observations on measured $\mathrm{Cu}_{\mathrm{sorbed}}$ (Table 7). The overall similar sorption capacities, despite different K_d values for the amendments, are attributed to the substantial contribution of PA sand to overall sorption and comparable ρK_{d-mm}values. This suggests that the summation approach of K_d for mixed media (i.e., ρK_{d-mm} by Eq. 3) reliably reflects sorption capacity of different media mixes. The difference in magnitudes between predicted and measured values may reflect (1) kinetic limitations at the "up" port, and (2) near-complete but incomplete exhaustion of the media.

A $\mathrm{Cu}_{\mathrm{sorbed}}$ value of 27.4 mg was predicted for the 10% Zeolite column due to the high zeolite ρK_d; however, only 6±0.8 mg was actually measured as sorbed. During the supplemental experiment where the infiltration rate through the 10% Zeolite columns was manually reduced from 183 cm/h to 73 cm/h using an outlet control, the residence time was increased to match or exceed that of other columns. In this experiment, $C_{\mathrm{eff\_up}}$ decreased from 59.8 to 58.2 µg/L, and C_{eff_down} from 39.6 to 35.9 µg/L, demonstrating concentration reductions by less than 10% although the infiltration rate was reduced by over 50%. This shows reduced Cu sorption in the 10% Zeolite column still occurred even when the residence time was comparable to that of other columns, reflecting the slower sorption rate of Cu to zeolite.

The analysis above demonstrated an approach for estimating the sorption capacity of engineered media, based on the additive properties of individual media components. Given the volume-based design of biofiltration BMPs, media ρ must be considered in addition to K_d derived from static systems. The measured Cu_{sorbed} was 54% for both PA sand and 10% Rogue, 51% for 15% RAC, and 22% for 10% Zeolite, compared to the predicted Cu_{sorbed}. The summation approach overestimates sorption capacity because it represents the maximum capacity under given influent concentrations, and may be most useful as a tool to compare different candidate media prior to BMP construction or conservatively plan for maintenance. The approach should only be applied when predicting capacity in the absence of kinetic limitations. As kinetic limitations become more pronounced during stormwater biofiltration (as was observed for the 10% Zeolite), a model that integrates hydraulics, transport, and sorption kinetics is necessary to reliably estimate sorption capacity and effluent concentrations.

This work highlights the need to extend the predictive framework based on sorption equilibrium to incorporate sorption kinetics when evaluating sorption in high-flow real-world biofiltration scenarios. The observations and findings from these experiments are particularly meaningful because the experimental design was intended to replicate field conditions in several ways: (1) the media depth follows local biofiltration designs[7,71]; (2) the media composition and size (and the ponding depth) control the infiltration rate[14]; (3) the background matrix and Cu concentration are realistic for urban stormwater runoff.

Conclusion and Future Research – Dissolved Cu

Based on the media characterization, batch sorption experiments of individual media components, and biofiltration column experiments with engineered media mixes, dissolved Cu sorption was examined for its application in stormwater biofiltration systems.

The main findings from this work are:

- Among the properties tested, CEC_X showed the strongest correlation (*r*=0.88) with K_d from batch sorption experiments conducted with simulated runoff derived from a parking lot. CEC_X is a commercially measurable property that quantifies exchangeable cations in the media. CEC_X can serve as a parameter to predict the sorption capacity of different media, informing component selection and engineered media design for dissolved Cu sorption in biofiltration systems.

- Column experiments revealed that, due to the volume-based design of biofiltration systems, sorption-related properties from media characterization and batch experiments need to be evaluated on a volume basis, rather than a mass basis, in order to provide predictive capacity for contaminant treatment processes.

- A volumetric sorption affinity (ρK_{d-mm}) can be used to predict the maximum sorption capacity under specific influent concentrations. The approach is useful for predicting and comparing the sorption capacity of engineered media in columns where kinetic limitations are not significant. When kinetic limitations become significant (e.g., in 10% Zeolite), models that account for sorption kinetics are necessary to reliably predict sorption capacity. This approach provides a promising pathway for scaling up from bench-scale experiments to column-scale predictions where field considerations are incorporated.

- PA sand, an ASTM-C33 compliant sand, removed 9.8±0.6 µg/cm^3 of dissolved Cu in the top 11.25 cm of its media depth. This was comparable to 10% Rogue and 15% RAC columns in terms of capacity. The low K_d of PA sand was compensated by its high bulk density, enabling it to contribute to 60% or more of the sorption in all columns tested in this study.

- Initial effluent concentrations from engineered media columns reflect the kinetics of dissolved Cu sorption to the media (before its capacity is utilized) at high infiltration rates (~ 50 to 150 cm/h). Data show that sorption kinetics can be influenced by the amendments even with relatively low mixing ratios (10-15% v/v).

Directions for future research include:

- While this study used dissolved Cu as a model contaminant, the finding on CEC_X's predictive capacity for sorption may be applicable to other heavy metals, such as Zn(II) and Pb(II). Moreover, the volumetric sorption capacity calculation for the column systems and the applicability of translating properties from bench-scale experiments to biofiltration systems can be extended to other contaminants.

- Further research is needed to identify and quantify the properties that govern the kinetics of sorption. This information can be integrated into the current approach for estimating Cu sorption, addressing the kinetic limitations observed in this study to improve predictions of dissolved Cu sorption in biofiltration systems.

- Field conditions introduce additional complexities. The findings on CEC_X and ρK_d from this study can be further tested in mixed contaminant scenarios (e.g., involving multiple dissolved metals) in field biofiltration BMPs to refine the predictive framework.

By addressing these areas, future research can better bridge the gap between laboratory findings and real-world performance, informing biofiltration system design for effective stormwater quality management.

LABORATORY EXPERIMENTS AND RESULTS ON PFAS

Introduction

Stormwater runoff has been identified as a key pathway for the migration of many contaminants of concern, including PFAS, into receiving water bodies.[36,32,37,46] Growing interest has emerged in assessing the effectiveness of stormwater BMPs for PFAS removal, particularly in water-stressed regions like California, where groundwater recharge using stormwater is a critical objective[81], while drinking water regulations for PFAS have been tightened[38].

Biofiltration (also known as bioretention) employs various blends of engineered media, mostly sand mixed with amendments, to treat stormwater quality. Given the recalcitrant nature of PFAS, sorption to engineered media is one of the few viable mechanisms for removing PFAS from stormwater. While many studies have investigated PFAS sorption across a range of water matrices[82,83,41,35,40,84,85], with a focus on materials like GAC and ion exchange resins[41,86,87], research specifically addressing PFAS removal from stormwater remains limited[13,88]. Two key differences need to be considered when applying PFAS sorption findings from other water matrices to stormwater: (1) stormwater is a complex chemical matrix containing a suite of co-contaminants, and (2) the choice of sorbent, i.e., media components, in biofiltration is constrained by cost and maintenance concerns, making materials such as GAC and ion exchange resins less viable.

To date, only a series of studies by the same research group have investigated PFAS sorption to engineered media using flow-through column experiments[14,79,89]. In their work, Pritchard et al. used breakthrough data from column experiments to demonstrate that sand amended with carbonaceous materials, including RAC and biochar, can remove PFAS from synthetic stormwater. Their modeling predicted that biofiltration systems using these media would have a lifetime of several decades in California. RAC and biochar, cost-effective alternatives to GAC, were chosen for their similar properties, including high specific surface area and relatively hydrophobic nature. Additionally, zeolite, a natural mineral alternative to cation exchange resins, was investigated in the initial study, although the ability to exchange anions is preferred for PFAS sorption.

The current study builds on previous research using column experiments to measure PFAS sorption to engineered media. The objective is to examine this process under conditions that more closely replicate field scenarios, including column structure, media selection and particle size, as well as the background runoff matrix. Biofiltration columns were constructed with four different engineered media and evaluated for their ability to remove two of the most prevalent PFAS compounds—PFOA and PFOS[10,12,33,46]. The engineered media included ASTM C33-compliant sand[65,66], used either alone or mixed with RAC, biochar, or zeolite. The long-term effectiveness of these media was tested by subjecting the columns to runoff under constant ponding depth, equivalent to 230—330 cm of cumulative rainfall, assuming the column surface area is equivalent to 5% of an impervious drainage area. For media that were effective for PFAS removal, the lifespan for PFOA and PFOS removal was estimated.

Materials and Methods

Runoff

Simulated stormwater runoff was generated for the column experiments to provide a reliable, repeatable supply of background runoff that mimics wet-weather conditions. Every 1—2 weeks, a section of the access road leading to a business complex parking lot (Figure 1), which had not received natural or simulated rainfall for at least one week, was sprayed with tap water. The created runoff was then directed to a curbside and collected. This runoff was pretreated to remove particulate matter through filtration using columns filled with VitroClean glass sand (Waterline Technologies, CA), which has a particle size range of 0.53—0.95 mm and a mean particle size of 0.74 mm. The pH of the pretreated runoff ranged from 6.0 to 7.5 and the TSS concentration was below the detection limit of 2 mg/L. The runoff was then spiked with PFOA and PFOS, each at 1000 ng/L, along with Cu at 50 µg/L and NO_3^--N at 1 mg/L, using stock solutions. Stock solutions were made from PFOA as a solid and 10 mg/mL PFOS in ethanol (both ≥95%, Cayman Chemical, MI), 1000 mg/L Cu standard solution in 1 M KNO_3, and 5 M $NaNO_3$ solution (Cole-Parmer, IL).

Column structure

The columns were constructed from transparent polyvinyl chloride (PVC), measuring 90 cm in length and 10 cm in diameter. The column structure and packing processes were designed to closely mimic biofiltration BMP installation[7,71]. A 5 cm layer of No. 8 washed stone (sizes ranging from 1.2 to 2.4 cm) and a 10 cm layer of No. 57 washed stone (2.5 to 3.8 cm) were included as the base layer to allow free drainage while preventing media washout. Forty-five cm of engineered media (typical of a field biofiltration facility in Southern California) were then packed into the columns in 15 cm increments through wet compaction. Two sampling ports (Figure 11) were installed at media depths of 11.25 cm (25% depth) and 40 cm (89% depth). Each column was equipped with a shower drain, funnel, and ball valve at the bottom for controlled drainage if needed. Each component of the drainage system at the base of the columns was tested individually to ensure it did not impede free drainage.

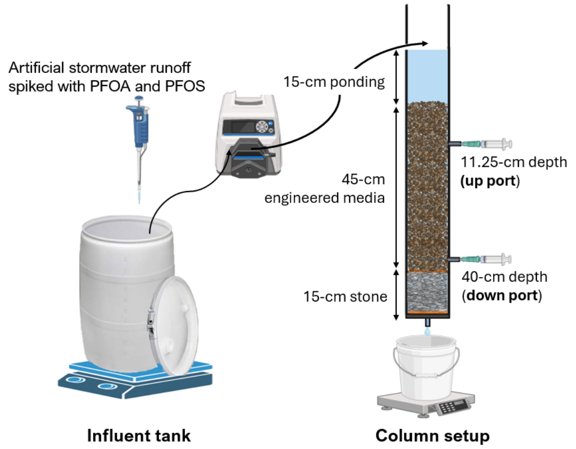

Figure 11. Diagram illustrating the column structure and sampling port positions

Engineered media

A total of eight columns were packed using four engineered media compositions, each in duplicate, as outlined in Table 9. The engineered media consisted of sand from a local supplier, Pacific Aggregates, CA (PA sand), which meets ASTM C-33 standards[65,66], either alone or mixed with an amendment at 10% or 15% (v/v). The amendments included Rogue biochar (a commercial wood-derived biochar from Oregon Biochar Solutions, OR), clinoptilolite zeolite (KMI Zeolite, NV), and RAC (Calgon Carbon, CA). The particle size distribution of the media was measured (Figure 12); the ranges (D10—D90) of PA sand, Rogue biochar, zeolite, and RAC are 0.33–2.05 mm, 2.12—5.35 mm, 1.33—3.72 mm, and 1.08—3.35 mm, respectively. The median particle sizes (D50) of these materials are 1.21 mm, 3.87 mm, 2.60 mm, and 1.70 mm, respectively. These sizes are representative of those expected in a local biofiltration BMP.

Table 9. Summary of column experiments

Column name	Media composition (by volume)	Mass percentage of the amendment	Infiltration rate (cm/h)	Loading rate[*] (cm/d)	Elapsed testing days	Elapsed calendar days
PA sand	PA sand only	—	58−127	180−340	21	55
10% Rogue	10% Rogue + 90% PA sand	0.8%	51−107	160−340	21	55
10% Zeolite	10% Zeolite + 90% PA sand	5.6%	56−183	240−380	24	58
15% RAC	15% RAC + 85% PA sand	5.6%	43−150	120−320	24	58

[*] The loading rate was represented by the daily runoff depth applied to the columns.

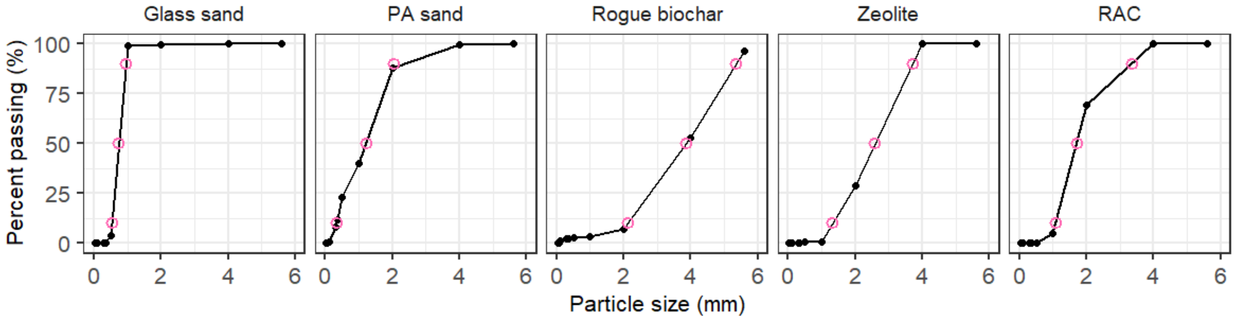

Figure 12. Particle size distribution of the media components used in this study, determined by sieving approximately 500 g of media through sieves with sizes ranging from 0.025 to 5.6 mm. The pink open circles represent the D10, D50, and D90 percentiles.

This column experiment is an extension of another study focused on dissolved Cu sorption and removal. Prior to the dosing condition and methods described herein, the PA sand and 10% Rogue columns had received 600—900 L of simulated stormwater runoff containing 50 µg/L Cu, 1 mg/L NO_3^--N, and 25 ng/L of both PFOA and PFOS. The amounts of PFOA and PFOS loaded to these columns are not expected to impact the results here, as the total loaded amount in the stormwater was only 10-16% of PFAS sorption observed in the 15% RAC columns.

Column experiments

The runoff was applied to the columns 2—4 days a week from June to July 2024. Daily operations maintained a constant ponding depth of 15 cm[73], regulated by an overflow outlet. The columns were operated in downflow mode for 1.5—3.5 h until the influent tank was exhausted each day, and they were fully drained at the end of each experimental day. Daily infiltration rates (Table 9) were calculated by monitoring the effluent collected in a bucket set atop a data-logging balance. The recorded effluent weight and sampling times were combined to track the total volume of runoff processed by the columns. Each column received a total of 350—600 L of runoff (additional runoff for the PA sand and 10% Rogue columns).

Sampling and analysis

Aqueous samples were collected daily from the influent tank and from the two sampling ports ("up" and "down") of each column (Figure 11). A 50 mL sample was extracted from the horizontal middle of the column using a 5-cm, 16-gauge needle connected to a 50 mL syringe. The samples were stored in a 50 mL polypropylene tube at 4 °C until analysis. Selected samples were analyzed for PFAS using EPA method 1633 by Physis Environmental Laboratories, Inc. (CA), which has reporting limits of 1.65 ng/L for PFOA and 1.92 ng/L for PFOS**.**

PFAS concentrations from the influent, as well as the mean concentrations from the "up" and "down" effluent sampling ports of both columns, were compared for each column using a paired Wilcoxon signed rank test with a Bonferroni adjustment for multiple comparisons. The analysis was conducted in R using the pairwise.wilcox.test function. This non-parametric test assesses whether the distributions of differences between groups are symmetric about zero. The Bonferroni adjustment provides conservative P values (ranging from 0 to 1), with lower P values indicating stronger evidence of different group distributions. A P value of <0.05 indicates a statistically significant difference.

Results and Discussion

The breakthrough curves of PFOA and PFOS for each column composition are presented in Figure 13, with the measured concentrations of both "up" and "down" effluent samples from duplicate columns plotted on the y-axis. The biofiltration columns received a PFAS-loaded cumulative rainfall of 230—330 cm (Figure 13, x-axis), assuming the column cross-section represented 5% of an impervious drainage area. This is equivalent to 6—13 years of rainfall based on an average annual rainfall of 25—38 cm/year[78] in Southern California.

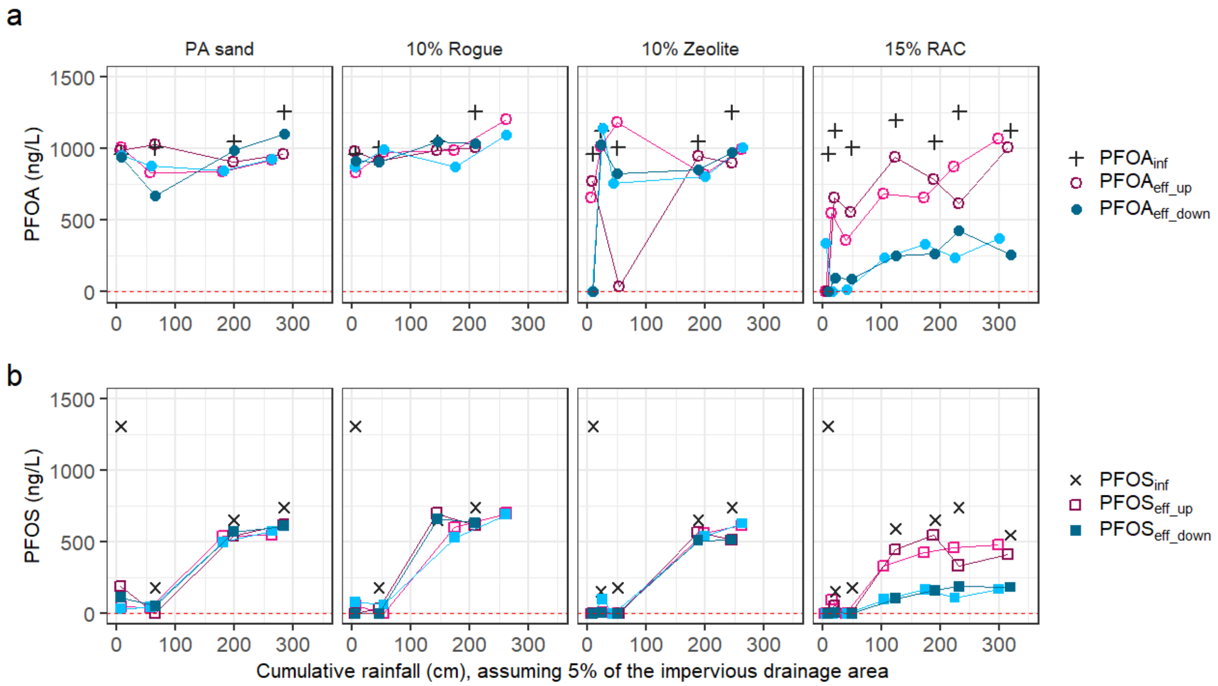

Figure 13. Breakthrough curves for (a) PFOA and (b) PFOS at the “up” and “down” effluent sampling ports of the biofiltration columns. Influent samples were collected directly from the tanks supplying all columns and applied to all panels, while effluent samples were taken from each port and column. Dark and light-colored symbols represent results from duplicate columns and red horizontal lines represent laboratory reporting limits. The pH of all effluent samples ranged from 7.19 to 8.20.

The average influent concentrations of PFOA and PFOS ($PFOA_{inf}$ and $PFOS_{inf}$) were measured at 1085±107 ng/L and 656±399 ng/L, respectively. These concentrations are higher than typical urban runoff (<100 ng/L[10,12,11,46]), but lower than those found near hotspot PFAS sources like fire training/response sites, landfills, and industrial areas, where concentrations can reach µg/L to mg/L levels[90,91]. The elevated concentrations used in this study were intended to stress-test the capacity and long-term effectiveness of the media, as well as to ensure that concentration differences could be calculated within the detection limits of quantification for these compounds. Variability in $PFOS_{inf}$ concentrations was observed, likely due to variations in spiking or analytical processes, such as sample extraction and surrogate recovery.

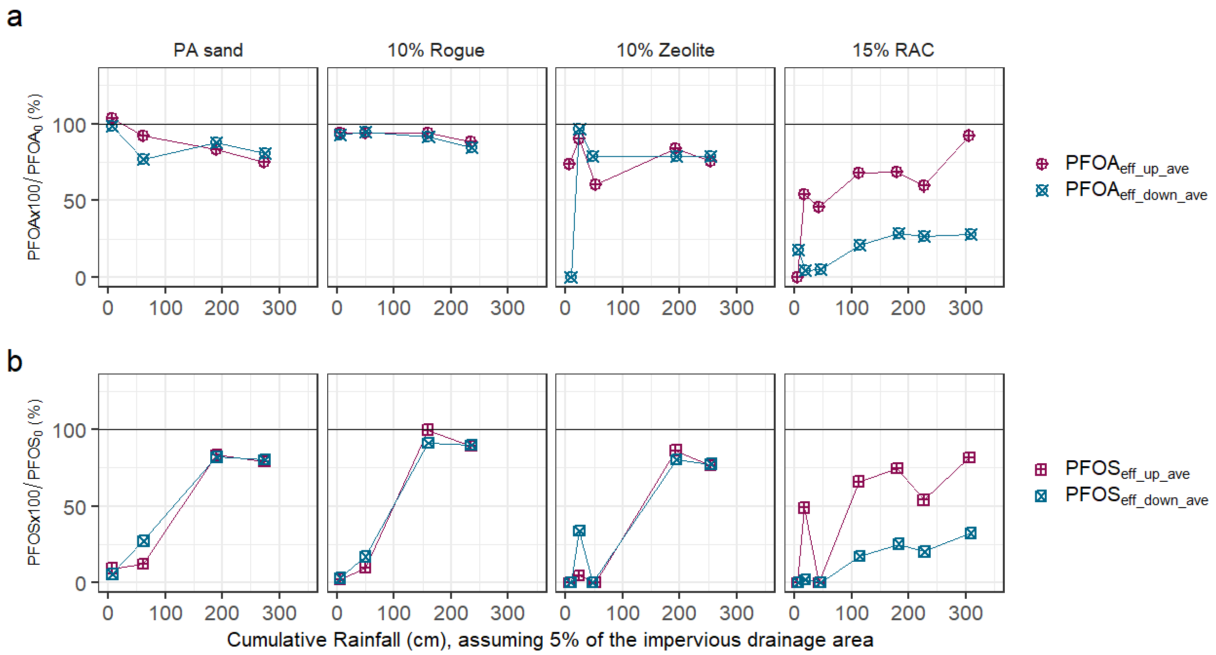

Figure 14. Breakthrough curves showing the percentage of (a) PFOA and (b) PFOS concentrations at the "up" and "down" effluent sampling ports, relative to their corresponding influent concentrations. Averages were calculated for PFOA and PFOS results, as well as for cumulative rainfall from the duplicate column measurements

PFOA effluent concentrations from PA sand and 10% Rogue ranged from 70—100% of the influent concentrations, showing that these columns were largely ineffective at sorbing PFOA (data are plotted in Figure 14). In contrast, PFOS effluent concentrations were <30% of the influent concentrations at the first two sampling events (Figure 14 (b)) but increased to >70% at the third sampling event after receiving 150 cm of cumulative rainfall. This suggests that PA sand and 10% Rogue columns were able to remove PFOS, albeit with limited capacity. For the 10% Zeolite columns, the exact cumulative rainfall treated is difficult to estimate due to gaps between sampling events, but both PFOA and PFOS were removed during the first 1—3 sampling events. Sorption to zeolite is thought to occur through hydrophobic interactions[87] or electrostatic interactions between the carboxylic/sulfonic groups of PFAS and the positively charged sites on the zeolite framework[32,92], despite zeolite being overall negatively charged.

Statistical analysis was performed to evaluate differences between influent and mean effluent concentrations of both columns, as well as between the mean effluents from the up and down sampling ports, for the overall datasets for each media composition. Results from the paired Wilcoxon analysis (Table 10) revealed significant differences ($P<0.05$) only for the 15% RAC columns, between the influent and "up" effluent, and between the influent and "down" effluent. Consistent with the statistical results, breakthrough curves showed that 15% RAC columns demonstrated more effective PFAS removal over a longer duration. For the down port, $PFOA_{eff\_down}$ and $PFOS_{eff\_down}$ from the first sampling were below reporting limits but increased to a steady state discharge of *ca.* 300 ng/L and 200 ng/L, respectively, by the end of sampling (307 cm of cumulative rainfall), indicating that the full column's capacity for PFOA and PFOS has not yet been reached. For the up port, $PFOA_{eff\_up}$ and $PFOS_{eff\_up}$ concentrations gradually increased, reaching 92% and 82% of their corresponding influent levels (1000 ng/L and 500 ng/L, respectively) by the end of sampling, demonstrating near-complete exhaustion at the up positions.

Table 10. P-values of the paired Wilcoxon signed rank test with a Bonferroni adjustment

Column name	$PFOA_{inf}$ vs. $PFOA_{eff\_up}$	$PFOA_{inf}$ vs. $PFOA_{eff\_down}$	$PFOA_{eff\_up}$ vs. $PFOA_{eff\_down}$	$PFOS_{inf}$ vs. $PFOS_{eff\_up}$	$PFOS_{inf}$ vs. $PFOS_{eff\_down}$	$PFOS_{eff\_up}$ vs. $PFOS_{eff\_down}$
PA sand	0.75	0.38	1.00	0.38	0.38	1.00
10% Rogue	0.38	0.38	0.75	0.38	0.38	1.00
10% Zeolite	0.19	0.19	1.00	0.19	0.19	1.00
15% RAC	0.047	0.047	0.094	0.047	0.047	0.177

Based on the exhaustion capacity from the up ports, the amount of PFOA and PFOS sorbed to RAC was calculated to be 1910 ± 97 ng/g and 1832 ± 35 ng/g, respectively, using Eq. 5 and data from Figure 13, under the assumption that PA sand does not contribute to PFAS sorption.

$$Sorbed\ amount\ (ng/g) = \frac{\sum(\overline{C_{inf}} - C_{eff_i}) \times v_i}{m_{RAC}} = \frac{\sum(\overline{C_{inf}} - C_{eff_i}) \times v_i}{25\% V_{media} \times 15\% \times \rho_{RAC}} \qquad \text{[Eq. 5]}$$

where $\overline{C_{inf}}$ (ng/L) is the mean influent concentration, C_{effi} (ng/L) is the effluent concentration at the ith sampling event from the up port, and v_i (L) is the volume of runoff processed by the column between the (i-1) and ith sampling events. m_{RAC} (g) is the mass of RAC in the column above the up port. The value of m_{RAC} is calculated using the total volume of the 45-cm media layer (V_{media}=3710 cm^3), the volume percentage of the "up" sampling layer (25%), the volume percentage of RAC in the media (15%), and the bulk density of RAC (ρ_{RAC}= 0.547 g/cm^3). Mean values were calculated from duplicate columns, with the range between duplicates representing the variability for each compound.

Extrapolating the 92% and 82% of exhaustion at 25% of the column depth to full column depths (45 cm) containing 15% (v/v) RAC suggests that 1335 cm and 1498 cm rainfall would be treated to reach exhaustion for PFOA and PFOS, respectively, assuming the biofilter has a surface area of 5% of an impervious drainage area. This corresponds to a lifespan of 35–59 years under local annual rainfall conditions (25—38 cm/year[78]). These estimates coincide with a previous study[89] that predicted a 51 ± 17-year lifespan for columns with 60 cm media containing 10% (v/v) RAC from a different vendor, using runoff containing PFOS under an average annual rainfall of 29 cm/year. The lifetime would be correspondingly reduced in areas with higher rainfall and could be extended by using greater depths and/or higher ratios of RAC.

In the current study, the infiltration rate of the RAC columns ranged from 43–150 cm/h (Table 9), which is at least twice as high as the 20 cm/h infiltration rate used in the referenced study. In a follow-up study where the infiltration rate increased from 20 cm/h to 40 cm/h, both PFOA and PFOS showed significantly faster breakthroughs, suggesting a kinetic limitation at 40 cm/h.[79] This implies that PFOA and PFOS sorption in the current study may also be kinetically limited under similar or higher infiltration rates.

The Rogue biochar columns were largely ineffective for PFAS removal; this contrasts to the referenced study where biochar columns only slightly underperformed compared to RAC columns. The ineffectiveness of the biochar columns could be due to (1) a lower volume percentage (10%) and, accordingly, a lower mass percentage (0.8%) of biochar, (2) the properties of biochar, and/or (3) a higher infiltration rate compared to the referenced study. If the latter is the primary factor, it suggests that Rogue biochar exhibits slower sorption kinetics than RAC and is more sensitive to infiltration rates.

The disparity in PFOS and PFOA removal may be attributed to the lower solubility of PFOS compared to PFOA, with solubilities of 680 mg/L for PFOS and 9500 mg/L for PFOA[93]. This difference results in greater mobility and less sorption of PFOA relative to PFOS, as evidenced by the initial sampling differences in PA sand and 10% Rogue biochar columns. Consistent with this, previous studies on PFAS sorption to carbonaceous sorbents in clean water matrices have shown higher breakthrough volumes for PFOS than PFOA with GAC[82], and an order of magnitude greater linear sorption coefficient (K_d) for PFOS than PFOA in biochars from wood or paper mill waste[83].

To gain further insights into the properties of the engineered media components that may lead to the differing performance across these columns, sorption-related properties (pH, cation exchange capacity, contact angle, and specific surface area) were assessed (Table 4). RAC exhibited the highest contact angle (71.9 ± 9.4°) among the four materials tested, followed by zeolite (62.6 ± 10.3°), while Rogue biochar and sand had much lower contact angles of 54.6 ± 14.7° and 53.6 ± 9.6°, respectively. Since RAC demonstrated significant PFOA and PFOS removal and zeolite showed some removal at least at the first sampling event, this suggests that the hydrophobicity of the media may influence the sorption of long-chain PFAS compounds such as PFOS and PFOA[85,87,94]. These observations underscore the need for further research to identify the properties of biochar and other amendments that can trigger PFAS sorption under varying infiltration rates in biofiltration systems.

Conclusions and Future Work - PFAS

This study assessed the PFAS sorption performance of four engineered media compositions in biofiltration columns. A simulated runoff was used, containing 1085 ± 107 ng/L PFOA and 656 ± 399 ng/L PFOS, treating an equivalent cumulative rainfall of 230—330 cm under high infiltration rates (43–150 cm/h). The findings include:

- Sand columns amended with 15% (v/v) RAC demonstrated effective removal of PFOA and PFOS, reducing influent concentrations of 1085±107 ng/L and 656±399 ng/L to 300 ng/L and 200 ng/L, respectively, after receiving a cumulative rainfall of 307 cm, assuming the biofilter surface area is equivalent to 5% of the impervious drainage area.
- The RAC sorbed 1910 ± 97 ng/g PFOA and 1832 ± 35 ng/g PFOS, based on exhaustion of the top 25% of media (11.25 cm depth) in 15% RAC columns, where the effluent concentrations reached 92% and 82% of influent. The estimated cumulative rainfall for complete breakthrough of the full column (45 cm) was 1335 cm for PFOA and 1498 cm for PFOS. This corresponds to a lifespan of 35–59 years under local annual rainfall conditions (25—38 cm/year).
- PA sand columns and PA sand mixed with 10% (v/v) Rogue biochar or zeolite were either ineffective or showed very limited capacity for PFAS removal. The ineffectiveness of the 10% Rogue was likely due to the low amendment mass ratio, the properties of this biochar, and/or high infiltration rate.
- The results suggest that the hydrophobicity of the media, measured by contact angle, may influence PFOA and PFOS sorption. Additional research is needed to confirm this initial finding.

The media overall performed better for PFOS sorption than for PFOA, which aligns with existing literature and reflects the lower solubility of PFOS. Future research should investigate which measurable properties of biofiltration media most influence PFOA and PFOS removal, and explore how these properties affect the treatment of both long and shorter-chain PFAS compounds under infiltration rates representative of field-installed biofiltration systems.

MECHANISTIC MODEL OF TREATMENT PROCESSES

The OpenHydroQual model was identified during the laboratory phase of the research as the most promising option to simulate the sorption treatment process in a biofiltration BMP. This section provides a literature review on the state-of-the-practice in stormwater quality modeling, leading to the selection of OpenHydroQual. Appendix B includes a slide deck presented to the STORMs unit, outlining the rationale for model selection and an introduction to OpenHydroQual.

Literature Review – Stormwater Quality Modeling

Overview of Stormwater Modeling at Multiple Spatial Scales

The objective of urban storm water management is to control the quantity and quality of runoff in built environments [95]. Devices that capture and treat storm water runoff, commonly called BMPs, are used to reduce the water quantity and improve the water quality[96]. Computer modeling in storm water allows for the impacts of proposed management strategies (including BMPs) to be assessed before costly infrastructural improvements are undertaken[97–100].

Water quality and BMP modeling typically occurs at three spatial scales, depending on the question of interest or stage of watershed planning and implementation (Figure 15):

- Watershed-scale modeling may be pursued to support beneficial use attainment or protection in the receiving environment, e.g., developing waste load allocations for total maximum daily loads (TMDLs), and coarse resolution planning for BMPs. Potential water quality improvements by BMPs are “lumped” together, i.e., pollutant removal is assumed for the watershed as a whole, ignoring factors such as specific loadings to the BMP, placement of BMPs within the watershed, or types of BMP.

- Subwatershed-scale modeling introduces finer spatial resolution than watershed scale modeling, and allows for improved calibration during the development of watershed management plans, assuming adequate data is available. Model calibration at a subwatershed scale may be used as a basis for scaling-up results across an entire watershed and allows for routing of flows through the watershed (which may include pollutant transformations and hydrograph attenuation), with the aim of reducing uncertainty in model predictions. BMPs may yet be lumped together, or distributed through the subwatershed, depending on the geographic extent of subwatershed being investigated and/or the resources available to conduct the modeling exercise. BMP pollutant removal is still usually considered at a coarse resolution.

- Site-scale modeling accounts for specific pollutant loads, BMP type, and placement. Site scale modeling is usually initiated as watershed planning moves into implementation for TMDL watershed management plans, and design of new and redevelopment projects under MS4 stormwater permits. A site-scale model may be applied to evaluate BMP alternatives and design configurations, depending on the technical rigor of the model being used. Site scale models often provide the most refined opportunities for calibration, again depending on available data.

- Modeling larger than watershed-scale is sometimes referred to as regional-scale or continental-scale[101]. Models of this geographical size can be important for riverine and estuary modeling[102], but rarely contain BMP features[103].

- Recent advancements in storm water simulation programs have significantly improved storm water quantity (a.k.a., hydrologic) modeling at nearly every scale, from continental-scale[101,104], through watershed-scale[105–107] to the BMP-site scale[108,109]. However, the rate of improvements for water quality simulation programs has not been as steep[110–114]. There are myriad reasons why water quality modeling may, in fact, be more difficult than water quantity modeling.

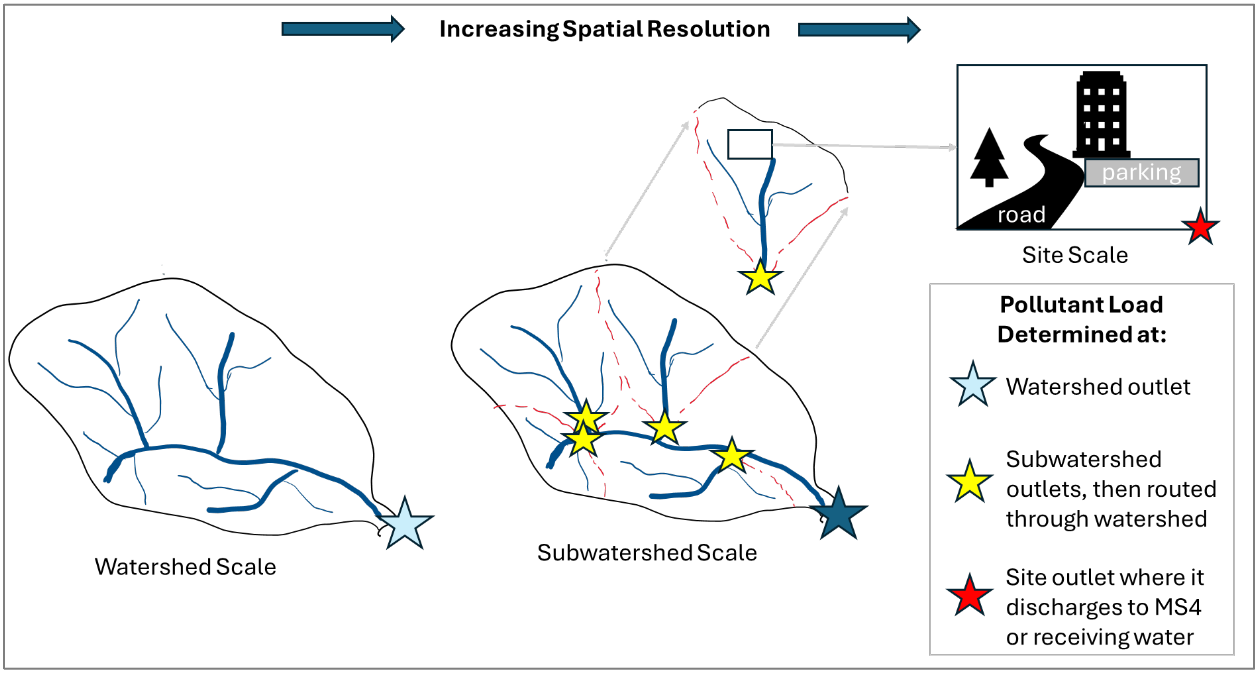

Figure 15. Schematic representing model configurations at three spatial scales: (left) watershed scale models determine pollutant loads at the watershed outlet; (middle) subwatershed scale models determine pollutant loads for individual subwatersheds, then route loads to the watershed outlet; (right) site scale models account for specific pollutant loads, BMP types and placement to determine pollutant loads where the site discharges to the MS4 or receiving water.

In all cases, successful water quality modeling (in terms of simulation program results that match observational data), presupposes successful hydrological modeling[115,116]; the mass of a pollutant is equal to the concentration (water quality) times the volume (water quantity) (Figure 16). Input data for hydrologic and quality modeling are known with different degrees of certainty. In hydrologic modeling, sometimes called rainfall-runoff modeling[117,118], rainfall is converted to runoff at each timestep through well-defined physical processes[108,119]. Rainfall data are precisely measured and extremely available[120]. The rainfall-runoff transformation may be modeled using empirical runoff coefficients that apply fixed relationships between the amount of rainfall and the fraction of that rainfall that converts into runoff depending on the land use/land cover and soil type. The most common runoff coefficients are known as Rational Method runoff coefficients and Curve Numbers that are used with the NRCS TR-55 method (USDA 1986). More sophisticated models implement physical processes accounting uniquely for infiltration and the formation of surface flows (such as the St. Venant Equations which are partial differential equations derived from the Navier-Stokes equations for conservation of mass and momentum [Rossman, 2010]).

In water quality modeling, the concentration of a pollutant in runoff is typically assumed to be a function of the land-type upon which the runoff is generated[99,121]. While land-use data are typically available[122], high resolution land-use studies for pollutant concentration data are more sparse[123,124]. The National Stormwater Quality Database is likely the largest readily-available repository of coupled land-use and EMC data for the USA (Pitt et al. 2018). A range of build-up and wash-off models have been developed to more accurately capture the concentration of pollutants in storm water runoff[125–129]. Developing data for calibrating water quality models often requires significant field monitoring campaigns (Simpson et al. 2023; Tiefenthaler et al. 2001) and lengthy and expensive laboratory analysis[114,130]. Coupled land-use-concentration data or build-up wash-off modeling to generate pollutant loads at any model spatial scale are options available in some commonly used stormwater modeling software packages, such as the US EPA Storm Water Management Model (SWMM, Rossman, 2010). Significant user-driven technical information is required to parameterize these functions. As a result of one or more of these factors, water quality simulation programs have lagged behind public perceptions of water quantity initiatives; stakeholders believe that initiatives intended to improve water quality are being underestimated by the models[131].

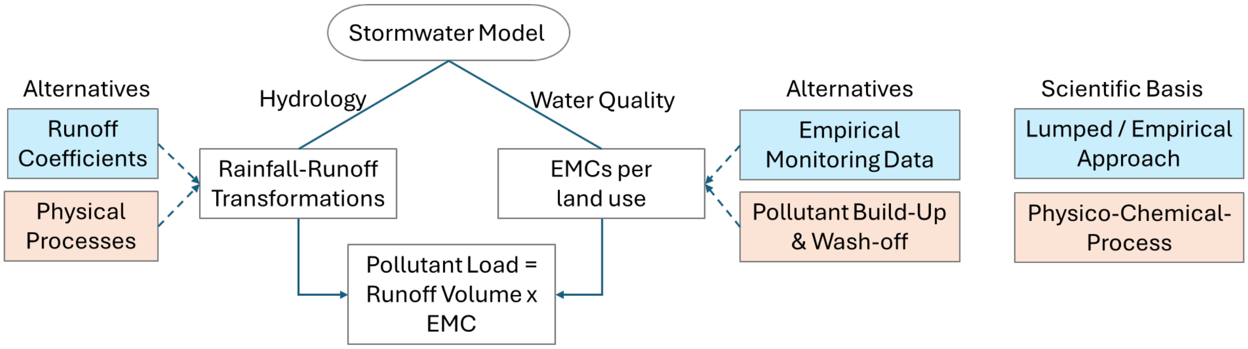

Figure 16. Conceptual representation of a stormwater model, including hydrology and water quality. The hydrology component implements rainfall-runoff transformations to generate runoff volumes. The water quality component applies event mean concentrations (EMCs) according to land uses represented in the model space. The pollutant load is the product of runoff volume and EMC.

BMP Water Quality Modeling

Many models offer only basic technical approaches for accounting for the effects of BMPs on runoff water quality. Modeling at the watershed and subwatershed scale often applies a user-defined %-reduction or %-removal type performance assessment to the BMP or suite of BMPs proposed. Pollutant reductions between the influent and effluent of the BMP are largely driven by reductions in effluent water *quantity* in some models[117,132,133], i.e., pollutant load reductions in BMPs that infiltrate, evapotranspire, or are harvested are due to the reduction in runoff volume discharged downstream rather than pollutant transformation or sequestration.

Computational modeling of the pollutant transformations within BMPs used to treat storm water has received inadequate attention, despite widespread BMP use. Some water quality models, such as the US EPA SWMM (Rossman, 2010), Hydrological Simulation Program – Fortran (HSPF, Bicknell et al., 2001) and System for Urban Stormwater Treatment and Analysis Integration (SUSTAIN, Lee et al., 2012) enable the user to assign a first-order decay regression to model pollutant transformations. In other words, the influent pollutant concentration exponentially declines as runoff flows through a BMP. This model is commonly applied in environmental engineering for estimating water quality treatment. Data to parameterize or calibrate this type of model as applied to BMPs is largely absent from the literature.

Obropta & Kardos (2007) spell out three approaches to modeling water quality within BMPs: deterministic, stochastic, and hybrid. Deterministic modeling seeks to capture the relevant physical and chemical processes with numerical solutions to dynamic equations[135–137]. Stochastic modeling, alternatively, leverages trends in the data to make predictions regarding future outcomes and design optimizations[138,139], sometimes invoking neural network techniques[140,141]. First-order regression models for pollutant decay in the US EPA modeling suite, fitted to empirical data, are considered herein to be consistent with a stochastic modeling approach[99,142]. Hybrid modeling blends deterministic and stochastic modeling. A key feature of hybrid modeling is the ability to incorporate parameter uncertainty in otherwise deterministic frameworks[105,127,143,144].

The research investigation described herein adopts a deterministic approach to modeling pollutant transformations within stormwater BMPs at the site scale. The deterministic approach is argued to be the more generalizable and accurate approach[115]. For biofiltration BMPs, the dominant physico-chemical interactions are filtration and sorption[114,145,146].

Some stormwater simulation programs address these mechanistic processes directly, such as the Micro-Pollutants in Raingardens model (MPiRe, Randelovic et al., 2016), HYDRUS-1D[147], and the Green Infrastructure Flexible Model (GIFMOD, Massoudieh et al., 2017). The MPiRe model numerically solves an adaptation of Darcy-flow infiltration model for fully saturated flow with first-order reaction kinetics and volatilization to specific heavy metals and fecal bacteria[149–151]. HYDRUS is a software package that couples the Richards' equation for variably saturated flow with non-equilibrium reactions between solid and liquid phases[147]. However, the tricky parameterization of the Richards' equation has led to sparing use for stormwater BMP modeling[135,152,153]. HYDRUS is proprietary software requiring a license to access and use. MPiRe and HYDRUS offer technically rigorous computation using well developed equations representing hydrologic and mechanistic treatment processes, but are currently applied mostly in the realm of academic research. Researchers have applied HYDRUS to simulating hydrology of BMPs including bioretention and green roofs. No water quality studies were identified, despite the program's potential application. The GIFMOD program [148] was originally presented as the fully deterministic foil to the US EPA suite of stochastic water quality models. It has since been adapted into the OpenHydroQual model[154].

OpenHydroQual

The OpenHydroQual model uses variably saturated storage blocks, advective-dispersive particle transport, and user-parameterized reaction (sorption) equations to couple water quantity with quality. OpenHydroQual is an open-source program available in a GitHub repository with a custom installation wizard. The model may be configured to simulate pollutant transformations within a BMP according to dynamic inputs, i.e., an influent hydrograph and pollutograph may be routed through the BMP to produce an effluent hydrograph and pollutograph. These data may be consolidated in post-processing into event mean concentrations (EMCs) and pollutant loads. Simulations can be conducted for single storm events, or in a continuous simulation representing multiple storm events interspersed with dry weather.

The model emerges as a good candidate for anticipated scenario testing. Its configuration includes specifying bioretention BMP properties including the depth, surface area, and physico-chemical properties of the media that influence sorption. A well-constructed model will enable applications to explore the interactions of media properties influencing sorption, depth and volume of treatment media, and ratios of candidate media components on effluent concentrations. For example, material A has 10x lower cation exchange capacity (the media property confirmed in the laboratory experiments to be a good predictor of sorption capacity) than material B, but costs 100x less. The model will enable evaluation of tradeoffs between using more of material A in lieu of material B while achieving the same level of performance but perhaps saving cost. The model can output event-to-event effluent quality, while tracking the build-up of pollutant within the media. In this way, long-term simulations will enable prediction in the deterioration in performance as exposure increases, as well as predict exhaustion of the media's capacity to remove pollutants by sorption. This type of information will help watershed managers better plan for BMP maintenance and understand implications for achieving downstream water quality goals. Finally, because the model can operate dynamically, it can be used to develop understanding of treatment sensitivity to various forcing functions (rainfall, flow, inflow concentrations/loads, BMP age, etc.), again yielding information that may be used to inform design.

Work Plan for Field Model Development

Introduction

Most structural BMPs are treated as a "black box". Untreated stormwater enters the BMP, treatment occurs, and then stormwater exits the BMP. This influent-effluent concept is the cornerstone of BMP performance monitoring. Managers expect that stormwater volumes and/or pollutant concentrations decrease from influent to effluent based largely on prior experience.

What treatment processes occur as stormwater flows through a structural BMP is not well studied and frequently unknown. Likewise, elements of BMP design related to water quality often follows rules of thumb, rather than science/engineering-based conditions to systematically induce treatment. The lack of process-based design and implementation contributes to widely variable and frequently unpredictable BMP performance.

Structural BMPs can facilitate a large variety of physicochemical and biological processes to capture stormwater and remove contaminants, with proper attention given to design specifications. These processes include, but are not limited to, infiltration, sedimentation, filtration, sorption, ion-exchange, oxidation/reduction, biodegradation, and phytoremediation.

The degree to which any of these elements is successful strongly depends on characteristics within the BMP itself, including characteristics of materials used (such as engineered media) and flow conditions (e.g., residence time, mixing or contact time with treatment materials) which are primarily controlled by media properties.

The aim of this research initiative is to identify and quantify the treatment processes for removing different pollutants of interest from stormwater within a structural BMP. The quantitative information on pollutant treatment and removal can then be utilized for optimizing structural BMP performance, setting rigorous design standards for structural BMP construction, and assessing when structural BMPs are not performing optimally and may require maintenance or retrofit.

Developing a process-based, mechanistic understanding of treatment directly leads to BMP design procedures that can guide engineers to match a pollutant to the appropriate treatment unit process (i.e., filtration, sorption, degradation, etc.). Ultimately, this will enable watershed managers – either regulators or regulated agencies – to choose the structural BMP design characteristics that best satisfies the water quality objective(s) with confidence that pollutant-specific treatment processes will support consistent performance.

Background

Project 3.1 Mechanistic Studies on Pollutant Removal by Stormwater Best Management Practices (BMPs) was ranked in the top 5 priority projects for the Southern California Stormwater Monitoring Coalition's (SMC) 2019-2024 Research Agenda. To fund the project, the scope was split such that the State Water Resources Control Board worked with the SCCWRP over the period 2023-2025 to design and execute a laboratory study, and develop an initial model. The SCCWRP project team, along with external advisor Professor Allen P. Davis (University of Maryland), provided updates to the SMC Steering Committee in quarterly meetings and presented findings of the laboratory study at the 2024 CASQA Conference in Sacramento. Two manuscripts are currently under review by prominent research journals and by SCCWRP's CTAG. The current phase of the project, for which the work plan herein is developed, is for the SMC to work with SCCWRP to extend the model from laboratory to field scale, and collect data to support model application at field scale.

Key decisions made during the laboratory phase of the project include first to focus on bioretention/ biofiltration type BMPs. Biofiltration BMPs (a.k.a. biofilters or bioretention) are among most commonly constructed BMPs in southern California. The pollutants targeted for testing in the laboratory included dissolved Cu and two of the most common PFAS, including PFOA and PFOS. These contaminants are selected because:

- These contaminants are among the least well studied in the BMP literature. The SMC Steering Committee prioritized selecting contaminants that are less well studied. In the case of bioretention, contaminants including Zn, phosphorus, nitrogen, and TSS have commonly been studied in both field and laboratory investigations.
- The focus is on dissolved contaminants because dissolved contaminants are likely to pose greater risk to receiving environments compared to those bound to stormwater particulates.
- The mechanisms for particulate removal by filtration are well understood compared to the anticipated treatment mechanisms of sorption for dissolved metals. Improving understanding of sorption processes in BMPs is relevant to design because the process can be predicted and manipulated according to physicochemical media properties.

A brief synopsis of the laboratory experiments completed 2023-2025 is as follows. The experiments were conducted to measure sorption of dissolved Cu and PFAS (PFOA and PFOS) in columns packed with sand and 3 mixed media blends (sand + amendments). Each column configuration was duplicated. Simulated runoff was created by washing a parking lot, filtering it to remove particulates, and spiking it with Cu(II) and PFAS. This process produced the resultant runoff representing a realistic background mixture while having targeted contaminant concentrations. Dissolved Cu and PFAS experiments were run in two phases: columns were subjected to runoff spiked with 50 µg/L of dissolved Cu and 25 ng/L of PFAS for an equivalent rainfall of 200-300 cm, and then runoff spiked with 50 µg/L of dissolved Cu and 1000 ng/L of PFAS for another 200-300 cm rainfall. The inflow to each column was regulated by maintaining a 15-cm ponding depth, as per typical field bioretention systems. Resultant flow rates were measured. Only one of the mixed media blends was temporarily successful at removing PFAS before reaching exhaustion (i.e., no further contaminant removal). Conversely, all four media removed measurable amounts of dissolved Cu; performance slowly declined for an equivalent of approximately 10 yrs' of rainfall prior to reaching exhaustion. Influent Cu was measured on 12 occasions over the duration of the experiment. Between 13 and 18 treated effluent concentrations were measured at two depths for each column, depending on column configuration, as well as total sorption capacity data.

Objectives and Scope

The primary objective is to configure, calibrate, and validate a mechanistic model predicting dissolved Cu removal by sorption to engineered media in biofiltration / bioretention. The model will initially be calibrated based on laboratory data collected during the initial phase of the project. The current project phase will collect field monitoring data, leveraging the SMC BMP Regional Monitoring Network, and use it to modify and apply the model, as appropriate.

The second objective is to use the model to evaluate design approaches and improve confidence in BMP performance predictions. This will entail developing and running applications to test scenarios of interest to SMC member agencies.

Excluded from the project scope is establishing a bioretention media testing or certification program, finding the “best” media, or writing new BMP guidance manuals.

Task 1. Convene working group

A working group consisting of SMC Steering Committee members or their designated representatives will be convened. The group is charged with:

- Reviewing and providing feedback on this work plan, model development, and model validation.
- Providing information on design and relevant aspects of the field condition of biofiltration BMPs monitored in the SMC BMP Regional Monitoring Network where data from those BMPs are used to support the modeling.
- Providing support through the SMC BMP Regional Monitoring Network for supplemental field data collection if/as required to support the modeling.
- Developing scenarios of interest to inform design and maintenance that can be evaluated with the model.
- Communicating with and engaging SMC Steering Committee representatives on project progress and outcomes.

The working group will meet on a milestone-oriented basis.

Task 2. Develop and calibrate a 1-D model for laboratory testing columns

The OpenHydroQual model was identified during the laboratory phase of the research as the most promising option to simulate the sorption treatment process in a biofiltration BMP. OpenHydroQual is an open-source program available in a GitHub repository. The priorities for model selection included an ability to incorporate variable inflow and pollutant concentrations, and explicitly represents pollutant treatment mechanistic processes, herein being sorption. Use of the model is intended for stormwater professionals with technical and quantitative expertise in BMP design.

OpenHydroQual may be configured to simulate pollutant transformations within a BMP according to dynamic inputs, i.e., an influent hydrograph and pollutograph may be routed through the BMP to produce an effluent hydrograph and pollutograph. An advection-dispersion-sorption model predicts pollutant treatment according to the physical and chemical properties of and flow rate through the media. Model predictions may be consolidated into EMCs and pollutant loads. The characteristics of the BMP may be explicitly represented, e.g., BMP surface area, engineered media depth and properties governing sorption capacity. Simulations can be conducted for single storm events, or in a continuous simulation representing multiple storm events interspersed with dry weather. A long-term simulation enables predicting the exhaustion of the BMP treatment capacity. A literature review describing the state-of-the-practice in stormwater quality modeling leading to selection of OpenHydroQual is provided in the previous section.

The model will be calibrated to simulate dissolved Cu treatment for up to two configurations of the column experiments that were completed during 2023-2025[iii]. The data described in the Background section are available to support the modeling. The two configurations will represent two different media. The primary purpose of modeling the column experiments include developing confidence that the model can accurately represent the system of interest where all conditions are known, as opposed to field conditions where multiple environmental and operational conditions may not be explicitly captured in data. A second purpose for modeling the columns is to provide a baseline for scaling up the models to represent field scenarios. Finally, modeling a physically smaller and simpler system like a laboratory column reduces the learning curve for configuring and running a model for a much more complex system such as encountered at field scale.

Metrics for evaluating model fitness will be developed in consultation with the working group. Candidate metrics include statistics such as R^2, Nash-Sutcliffe efficiency, and/or root mean square errors (RMSE). A sensitivity analysis will be performed to identify the relative impact of measured and calibrated parameters on model predictions for EMCs and sorption capacity. Evaluation of these outcomes will be considered by the working group to set expectations for model success.

Task 3. Collect field data to inform model

SMC member agencies currently collect field scale flow-through bioretention water quality data as participants in the SMC BMP Regional Monitoring Network. Existing data include influent and effluent flow-weighted EMCs, influent and effluent hydrographs, surface infiltration rate during storm events, and precipitation hyetographs. Many of the BMPs are currently in the 3rd season of sample collection. The existing effort is outlined in the SMC BMP Regional Monitoring

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[iii] PFAS will not be modeled. Data from column tests showed very limited potential for any of the media tested to remove PFAS. In addition, the very limited information currently available in the literature on PFAS in urban runoff suggests concentrations are at or near detection limits, thus the expense of sampling for PFAS is not justified at this time.

Network Work Plan (2022) and the QAPP (approved by the SMC working group Jan. 2023). Flow-weighted composite samples are analyzed for a range of pollutants. At a minimum according to the Work Plan, the analytical parameters should already include flow-weighted EMCs of total and dissolved Cu and Zn, TSS, total and ortho-phosphate, total nitrogen, nitrate + nitrite, and fecal indicator bacteria. The specific effort varies by participating agency.

Limited supplemental sampling is described herein to support the modeling. Supplemental data from up to two field BMPs include collecting two pollutographs during 2025, weather-permitting. Pollutographs are generated from collecting and analyzing grab (discrete) samples periodically over the hydrograph duration. Data must be from influent and effluent monitoring stations during the same storm event for a single BMP (i.e. the same event does not need to be sampled at BMP A and BMP B, but at BMP A both influent and effluent data are required for storm 1 and storm 2. Influent and effluent from BMP B can be sampled during the same or different storms). Ideally, pollutographs should be obtained for dissolved Cu, hardness, TSS, dissolved organic carbon, temperature and pH. As the laboratory cost is typically the same whether one metal or a suite of heavy metals are analyzed, additional analysis are suggested to complement the full suite of heavy metals being measured as EMCs at each BMP as part of the SMC BMP Regional Monitoring Network program. Preference should be given to parameters that directly support model interpretation in the context of the existing TMDLs in member agency jurisdictions. Specific decisions regarding additional analytical parameters will be made in a timely manner through consultation with the member agencies conducting monitoring, and the working group as needed.

The supplemental water quality samples (i.e., grab samples to support pollutographs) are to be collected concurrently with the influent and effluent hydrographs, surface infiltration rate, and precipitation hyetograph. All of these hydrologic parameters are already being collected as part of the SMC BMP Regional Monitoring Network. There is no change to how those hydrologic data are collected.

Media samples from the field BMPs will be collected by SCCWRP, with permission from the relevant member agency, for analysis of media properties relevant to the model development, for example, CEC, existing concentrations (i.e. background concentrations) of sediment-attached, extractable heavy metals, particle size distribution, hydraulic conductivity, and hydrophobicity.

Detailed data from two BMPs are recommended to increase the likelihood of ensuring data are suitable for model application. For example, measured extreme concentrations or flow rates – too low or too high – might skew model calibration. Preference is identified as BMPs with vertical sidewalls and without pre-treatment in order to promote generalizable results, and minimize site-specific features that might promote preferential flow paths or be poorly represented in a model. SCCWRP will work through details of pollutograph sample collection with individual member agencies since each member agency's equipment configuration differs. Procedures will be documented to include in reporting. Supplemental analytical costs for pollutographs will be covered by this project.

Contingency Plan: In order to meet the schedule for the project, pollutographs must be sampled by no later than December 2025, with hydrograph and analytical results available no later than the end of January 2026. SCCWRP will work with member agencies who conduct sampling on a storm-by-storm basis to evaluate whether anticipated storms might be suitable for pollutograph sampling. Should insufficient pollutographs be successfully sampled by November 2025, the research team will explore feasibility of conducting a synthetic field-scale storm event. Final decisions on the scope and procedures of a synthetic test, if pursued, will be made in consultation with the working group and will be documented in reporting, as appropriate.

Task 4. Field model development

The OpenHydroQual model developed based on the laboratory column experiments will be scaled to simulate one BMP from the SMC BMP Regional Monitoring Network. The key question to investigate is whether the model built on laboratory data accurately predicts or forms an appropriate analogy to field performance. At a minimum, the field model will be configured for simulating dissolved Cu treatment. Up to two additional parameters (e.g. dissolved Zn and other pollutants likely removed by sorption) can be simulated depending on data and resource availability.

Metrics for evaluating model fitness will be developed in consultation with the working group. Candidate metrics include statistics such as R^2, Nash-Sutcliffe efficiency, and/or RMSE. A sensitivity analysis on the field model will be compared to the model based on laboratory columns. Uncertainty will be quantified.

Task 5. Apply model to inform design

SCCWRP will work with the working group to develop scenarios of interest for exploring BMP design and implementation using the model. For example, an application scenario might evaluate tradeoffs between engineered media depth versus BMP surface area versus media properties, etc. Another application might evaluate the treatment potential according to varying media component ratios, as the laboratory experiments suggest a linear increase in volumetric media addition doesn't necessarily translate into a linear increase in performance, i.e., twice as much biochar doesn't mean twice as much treatment. Up to 3 scenarios will be explored using the model, depending on the scope of each scenario.

Schedule

Task	Deliverable	Completion Date
1 Advisory committee meetings	Online meetings scheduled on a milestone basis	5/31/2026
2 Develop and calibrate 1-D model	Technical memo	8/30/2025
3 Collect field data to inform model	2 x pollutographs and 2 x hydrographs for influent and effluent at 2 x BMPs	12/31/2025*
4 Field model development	Presentations to Advisory Committee and Steering Committee	3/31/2026
5 Apply model to inform design	Technical memo	6/30/2026

* At least one data set from each BMP must be collected in winter-spring 2025 to adhere to the remaining schedule. Criteria for model validation may be revisited in the absence of timely requisite data.

PRESENTATIONS TO THE STATE WATER BOARD

- Presentation on model selection (February 4, 2025)-Appendix B
- Presentation on pilot testing results (May 24, 2024)-Appendix C
- Presentation on the selection of BMPs and contaminants (June 30, 2023)-Appendix D

TECH TRANSFER ACTIVITIES

- 5 quarterly updates (including one extended presentation) to the SMC Steering Committee (since June 2023)-Appendix E

- 2024 California Stormwater Quality Association (CASQA) Conference presentation (October 2024)-Appendix F
- 2025 National Monitoring Conference presentation (March 2025)-Appendix G

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APPENDIX A. ANNOTATED LITERATURE REVIEW ON DISSOLVED COOPER AND PFAS

Appendix A

Task 22.2

Annotated Literature Review: Quantitative Evaluation of Pollutant Treatment Processes

Scope of the literature review

A review of best management practices (BMP) and stormwater databases and peer-reviewed articles was conducted. While all information from the databases and peer-reviewed articles is synthesized in “Literature Review and Workplan”, the peer-reviewed articles are fully annotated below to provide more detailed information.

The articles are organized categorically by pollutants:

1. Copper (p. A1)
2. PFAS (p. A8)

Studies that presented useful information on the design and operation of columns are noted in the Methods section of each study. The articles within each category are arranged in chronological order.

Articles critical to forming hypotheses and developing work plans are annotated separately.

3. Media properties and column operations (p. A21)

The literature review is intended to identify (1) the key mechanisms and processes for the removal of targeted pollutants, including Cu and PFAS, by biofiltration and (2) knowledge gaps in the context of stormwater and biofiltration for each pollutant.

The literature review is intended to help focus laboratory efforts on the treatment processes and experimental conditions that are most important, in order to prevent duplication of effort, shorten testing time, and prioritize tasks.

Copper (Cu)

1. **V. K. Gupta. 1998. Equilibrium Uptake, Sorption Dynamics, Process Development, and Column Operations for the Removal of Copper and Nickel from Aqueous Solution and Wastewater Using Activated Slag, a Low-Cost Adsorbent. *Industrial & Engineering Chemistry Research* 37(1):192-202. https://doi.org/ 10.1021/ie9703898.**

Objective

The objective of this study is to assess the effect of particle size distribution, contact time, and surface loading of Cu and nickel ions on the performance of adsorbent at the optimum pH (pH at 5 for Cu^{2+} and 4 for Ni^{2+}).

Methods

Batch experiments were conducted to obtain rate and equilibrium (isotherm) data. pH from 2-8 and temperature from 30-50 °C were investigated. Column studies were also carried out and a bed-depth-service-time (BDST) model was applied to the data obtained from the column studies.

Main findings

Based on batch and column experiments and reusability tests, the authors concluded that the activated slag is an effective adsorbent for the removal of Cu^{2+} and Ni^{2+} from wastewater. Through kinetic analysis, the authors determined that the rate-limiting step was particle diffusion. Regeneration of the material was possible with 1% HNO_3.

Limitations

As the study was designed in the context of wastewater, the initial concentrations of metals are at a mM level, much higher than the presence of Cu^{2+} in stormwater runoffs.

The study focused on a specific sorbent but not on why the sorbent is desirable.

Relevance

This classical study investigates many aspects of metal sorption to a sorbent – from batch study to column study, from equilibrium to rate, from thermodynamic calculation to kinetic modeling, pollutant competition, and regeneration of the sorbent.

For using a BDST model, data collected from different bed depths and flow rate data will be needed.

2. **C. Gabaldón, P. Marzal, A. Seco, J. A. Gonzalez. 2000. Cadmium and Copper Removal by a Granular Activated Carbon in Laboratory Column Systems. *Separation Science and Technology* 35(7):1039-1053. https://doi.org/ 10.1081/SS-100100209.**

Objective

This study aims to understand the single and competitive removal of Cd and Cu from aqueous solutions by a granular activated carbon through column experiments.

Methods

Seven experiments were conducted by varying the initial pH and flow rate. Each cycle of column experiments included three steps: pH precondition, tracer injection, and metal adsorption until column exhaustion occurred. Columns were run in an up-flow mode. Tracer tests were done using a KCl solution adjusted to a pre-determined pH.

Main findings

The study showed that metal removal was dependent on influent pH but not on flow rate under experimental conditions. The sorption of Cu outcompeted that of Cd in a combined system. The study reported a higher sorption capacity from column experiments than that from batch experiments, which was attributed to the higher concentrations used in the column experiments. Under the assumption that pore-diffusion was the rate-limiting step, the diffusion model well-predicted the initial zone of the breakthrough curves but failed to predict the tail zone of the curve.

Limitations

There was no information on the physicochemical properties of granular activated carbon. It also focuses on one media and thus no investigation into how the removal was affected by its property or other media.

Relevance

This study investigated the role of pH in metal adsorption. A tracer test was done to understand the hydraulic aspect of the column experiments.

3. R. Han, L. Zou, X. Zhao, Y. Xu, F. Xu, Y. Li, Y. Wan. 2009. Characterization and Properties of Iron Oxide-Coated Zeolite as Adsorbent for Removal of Copper(II) from Solution in Fixed Bed Column. *Chemical Engineering Journal* 149(1-3):123-131. https://doi.org/10.1016/j.cej.2008.10.015.

Objective

This study aims to evaluate the performance of iron oxide-coated zeolite (IOCZ) columns for the removal of Cu^{2+} from an aqueous solution using a fixed bed column.

Methods

IOCZ was characterized using SEM, FTIR, XRD, and BET analyses. The breakthrough curves were analyzed using three classical kinetic models, including the Thomas model, the Adams-Bohart model, and the bed-depth service time analysis model. Parameters from isotherm, obtained through batch experiments, were used to estimate the breakthrough curve.

Main findings

The study found that the adsorption of Cu^{2+} was strongly dependent on the flow rate, the initial concentration, and bed depth. For the modeling of experimental data, the Thomas model performed better than the Adams-Bohart model.

Limitations

Again, the study focuses on one media matrix and its performance. It Is difficult to delineate why the column or media performs the way in the study. The study evaluated the applicability of different models but didn't explain why one model performs better than the other.

The initial concentrations of metals are at a mM level, which was much higher than the presence of Cu^{2+} in stormwater runoffs.

Relevance

The study used three models, the Thomas model, the Adams-Bohart model, and a mass transfer model to fit the breakthrough curves and used the bed depth service time model to predict the performance of the column under different operating conditions. These models can potentially be applied to our results.

4. **A. Thomas, L. Haselbach, C. Poor, M. Freimund. 2015. Long-Term Metal Retention Performance of Media Filter Drains for Stormwater Management. *Sustainability* 7(4):3721-3733. https://doi.org/10.3390/su7043721.**

Objective

This study aims to investigate the long-term effectiveness of media filter drains for stormwater management through a column study.

Methods

A couple of media, which were aged to different extents, were collected from the field and used to construct columns. Media were collected from two sites—one vegetated and aged for 12 years and the other non-vegetated and aged for 5 years—at three depths (upper, middle, and bottom 100 mm). Six columns were constructed in total. The columns were subjected to highly concentrated solutions to simulate additional years of use.

Main findings

Through the accelerated aging events and the high-performance loading tests, the study concluded that the existing, aged media could be used to remove Zn^{2+} and Cu^{2+} in the long term (<10 years). The medium with a vegetation cover showed better performance despite its longer age and higher potential loading due to heavier traffic.

Limitations

It would be better if the study measured some physical properties of media and connected them to the performance of the columns.

Relevance

Field-aged media was used for lab column experiments and the performance of the field-aged media was evaluated for long-term use.

5. **K. Lange, Ö. Heléne, M. Viklander, M. Viklander, G.-T. Blecken. 2020. Metal Speciation in Stormwater Bioretention: Removal of Particulate, Colloidal and Truly Dissolved Metals. *Science of The Total Environment* 724: 138121. https://doi.org/10.1016/j.scitotenv.2020.138121.**

Objective

This study aims to quantify the treatment effectiveness of bioretention columns for dissolved metal species in stormwater.

Methods

The study employed a 0.45 µm filter and 2-kDa ultrafilter to divide metals into particulate, colloidal, and truly dissolved fractions. Targeted metals include Cu, Pb, Cd, and Zn. The study also investigated the effect of salts and plants on metal removal. The study used 1-m high and 0.11-diameter columns.

Main findings

The study revealed that while the total removal of metals was often high, the removal of colloidal and dissolved Cu and Zn was significantly lower. Due to the preferential removal of different metal species by biofiltration, colloidal and truly dissolved fractions were more prevalent in the effluent rather than in the influent. Salt affected metal removal mostly negatively, while vegetation had no significant effects.

Limitations

The study did not investigate the mechanisms through which the specific fractions of metals are removed, even though the study aims to understand the removal of each fraction by biofiltration. It was also unclear how important it is to differentiate colloidal and dissolved metals.

Relevance

The study identified that vegetation had mostly no significant effects on metal removal and fractionation. The study also highlighted the importance of the effective removal of dissolved metal species.

6. **T. Mehmood, J. Lu, C. Liu, G. K. Gaurav. 2021. Organics Removal and Microbial Interaction Attributes of Zeolite and Ceramsite Assisted Bioretention System in Copper-Contaminated Stormwater Treatment, *Journal of Environmental Management* 292: 112654. https://doi.org/10.1016/j.jenvman.2021.112654.**

Objective

The objective of this study is to evaluate a media mix, i.e., zeolite and ceramsite, the components of which possess different cation exchange capacities, surface characteristics, and organic matter content. The performance of the media was compared against the control with respect to Cu removal, microbial response to the Cu retained in the media, and the removal of organic carbon.

Methods

The columns consisted of a planting layer, soil layer, filler layer, filtration layer, and drainage layer, with the corresponding thickness of 5, 10, 30, 3, and 2 cm, respectively. Synthetic stormwater was prepared with and without 1 mg/L Cu. Dissolved O_2, total organic carbon (TOC), chemical oxygen demand (COD), pH, and organic carbon content were measured for aqueous samples, and microbial analysis was done for soil samples.

Main findings

Soils had excellent Cu retention over *ca.* 120-day testing, and filters removed additional Cu. Cu was retained mainly in the soil layer, suggesting the capacity of the filter was not fully exhausted. The main finding of this study was that the retention of Cu in the column affected microbial growth and TOC removal.

Limitations

The study failed to delineate the contribution of soil and each filter material, i.e., zeolite and ceramsite, for the removal of Cu, due to lack of control. The study didn't connect the properties of media and the removal capacity of media for Cu or organic carbon removal.

Relevance

The study tested Cu removal by soil and filter materials in field conditions, e.g., with temperature fluctuation.

7. **N. Al-mahbashi, S. R. M. Kutty, A. H. Jagaba, A. Al-Nini, M. Ali, A.A.H. Saeed, A. A.S. Ghaleb, U. Rathnayake, H. Nguyen. 2022. Column Study for Adsorption of Copper and Cadmium Using Activated Carbon Derived from Sewage Sludge. *Advances in Civil Engineering*. https://doi.org/10.1155/2022/3590462.**

Objective

The objective of this study is to assess the effectiveness of sewage sludge-based activated carbon for the removal of two metals, Cu and cadmium, from aqueous solutions through column experiments.

Methods

The BET surface area and pore size distribution of the activated carbon were characterized. The columns were in 1.5 cm diameter. The initial concentrations of the solution were 100 mg/L for each metal and the downflow rate was set at 2 mL/min. The solution pH was set at 5. Breakthrough curves were obtained at different bed depths (3, 6, and 9 cm) of columns. The breakthrough curves were analyzed and compared using three classical adsorption kinetic models, including the Adams-Bohart, Thomas, and Yoon-Nelson.

Main findings

Cu had the breakthrough later than cadmium. When the performance of three adsorption kinetics was compared, the Adams-Bohart model described only the initial part of breakthrough curves. Yoon-Nelson model and Thomas model were identified to well describe Cu and cadmium data, respectively.

Limitations

The study focused on one media but lacked benchmarking when evaluating its performance. The work compared different kinetic models and evaluated their performance but didn't explain why one performs better than the others.

The initial concentrations of metals are at a mM level, which was much higher than the presence of Cu^{2+} in stormwater runoffs.

Relevance

Three adsorption kinetic models were applied to reveal the sorption behavior of copper. It seems the Adams-Bohart model is consistently not performing well in estimating Cu sorption kinetics.

8. **W.-S. Chen, Y.-C. Chen, C.-H. Lee. 2022. Modified Activated Carbon for Copper Ion Removal from Aqueous Solution. *Processes* 10(1). https://www.mdpi.com/2227-9717/10/1/150.**

Objective

This study aims to compare activated carbon derived from wood materials —activated carbon, activated carbon modified with HNO_3, and activated carbon modified with HNO_3 and iminodiacetic acid— for Cu^{2+} sorption through batch and column studies and modeling on equilibrium and kinetic aspects.

Methods

HNO_3 was used to increase functional groups of activated carbon and iminodiacetic acid was added to the activated carbon to act as a chelating agent. A suite of characterization was conducted on the unmodified and modified activated carbon, including FTIR, elemental analysis, SEM, BET surface area, pore structure analysis, Boehm titration, and pH point of zero charges (pH_{ZPC}). Batch sorption experiments were conducted at three temperatures (298, 308, 318 K) to obtain isotherm and thermodynamic parameters.

Main findings

By modifying the surface of activated carbon with HNO_3 and iminodiacetic acid, the adsorption capacity increased from 25.04 mg/g to 53.99 mg/g and 83.75 mg/g, respectively. The addition of iminodiacetic acid also promoted the removal of Cu^{2+} at low concentrations. The study attributed the increased removal of Cu^{2+} to the increase in oxygen-containing functional groups of AC.

Limitations

While the amount of oxygen functional groups may have increased, porosity and BET surface area decreased and pH_{ZPC} increased with iminodiacetic acid modification. It is difficult to understand the interplay between these characteristics of media for Cu^{2+} adsorption.

Relevance

The study focused on a few media and investigated their characteristics and performance in batch and column experiments.

9. **S. Spahr, M. Teixidó, S. S. Gall, J. C. Pritchard, N. Hagemann, B. Helmreich, R. G. Luthy. 2022. Performance of Biochars for the Elimination of Trace Organic Contaminants and Metals from Urban Stormwater. *Environmental Science: Water Research & Technology* 8(6): 1287-1299. https://doi.org/10.1039/D1EW00857A**

Objective

This study aims to improve biochar selection process for the removal of metals and trace organic contaminants from urban stormwater and identify trace organic compounds that can serve as indicators for the performance and longevity of biochar filters.

Methods

Three biochars were prepared from a mix of spruce and fir wood at different temperatures (200, 580, 750 °C, respectively). Another biochar was prepared from conifer softwood through gasification at temperatures up to 1100-1400 °C. Biochars were screened for sorption of metals and trace organic contaminants through separate series of batch experiments. BC750 and MCG biochar (gasification biochar) were evaluated with respect to sorption of both heavy metals and trace organic contaminants. Column experiments were then evaluated with different amounts of carbonate sand and MCG biochar, and a 1-D intraparticle diffusion model was applied to predict the breakthrough of trace organic contaminants in filters.

Main findings

Batch experiments showed that the removal capacity of biochars increased with increasing specific surface area. Among seven organic compounds evaluated, dicamba exhibited early breakthrough, consistent with poor retention of anionic organic compounds in biochar.

Limitations

Specific surface area, ash content, and elemental compositions were the only properties measured for the biochars. The wet/dry seasonal operation was beyond the scope of the study.

Relevance

The study investigated the sorption of both metals and trace organic contaminants. The 1-D intraparticle diffusion model might be applicable to our study.

PFAS

1. **P. McCleaf, S. Englund, A. Östlund, K. Lindegren, K. Wiberg, L. Ahrens. 2017. Removal Efficiency of Multiple Poly- and Perfluoroalkyl Substances (PFASs) in Drinking Water Using Granular Activated Carbon (GAC) and Anion Exchange (AE) Column Tests. *Water Research* 120: 77-87. https://doi.org/10.1016/j.watres.2017.04.057.**

Objective

The objective of this study is to investigate the effects of PFAS chain length, functional group, and isomer structure on the removal of multiple PFASs by GAC and AE columns.

Methods

The removal of 14 different PFAS compounds with different chain lengths and functional groups was monitored for a 217-day period. After each sample collection, the columns were backwashed for 2-6 min using a pump.

Main findings

A clear relationship between perfluorocarbon chain length and removal efficiency of PFASs was found for both GAC and AE columns. PFASs with sulfonate functional groups displayed greater removal efficiency than those with carboxylate groups. Shorter carbon-chained PFASs such as PFBA, PFPeA, PFHxA showed desorption behavior towards the end. Long-chained PFASs showed increased removal towards the end, indicating agglomeration or micelle development. Linear isomers of PFOS, PFHxS, and perfluorooctane sulfonamide (FOSA) had greater removal than the branched isomers. The GAC and AE columns showed a poor correlation between DOC and PFAS removal efficiency.

Limitations

The tests were run in the context of drinking water and small-size columns were used. Concentration was used to calculate removal efficiency instead of masses.

Relevance

A clear comparison was made between GAC and AE with respect to PFAS removal. The study was run for a relatively long time.

2. **M. Ateia, A. Alsbaiee, T. Karanfil, W. Dichtel. 2019. Efficient PFAS Removal by Amine-Functionalized Sorbents: Critical Review of the Current Literature. *Environmental Science & Technology Letters* 6(12): 688-695. https://doi.org/10.1021/acs.estlett.9b00659.**

Objective

The review intends to provide a critical analysis on the development and application of amine-containing sorbents for PFAS removal. The review also provides an outlook on the key areas of research needed to develop more efficient sorbents.

Methods

The review started with an introduction on aminated sorbents and was organized by listing factors affecting PFAS removal by aminated sorbents and the mechanism and kinetics of PFAS adsorption on aminated sorbents, and then discussed challenges in the application of current aminated sorbents and suggested the way moving forward.

Main findings

The review evaluated sorbents based on scalability, recyclability, synthetic tunability, removal rates, and removal capacity. The review identified initial PFAS concentrations, headgroups and chain lengths, and the coexistence of background contaminants as the factors affecting PFAS removal from aqueous phase. The review also summarized that the removal mechanisms of PFAS by aminated sorbents rely on the combined effects of electrostatic interactions, hydrophobic interactions, and morphology (e.g., shape, size) of the sorbent, and the interplay between these interactions.

Limitations

Aminated sorbents are not media commonly used in stormwater treatment.

Relevance

The review provides a clear explanation of the physical properties of PFAS and the removal mechanisms of PFAS by aminated sorbents.

3. **C. Zeng, A. Atkinson, N. Sharma, H. Ashani, A. Hjelmstad, K. Venkatesh, P. Westerhoff. 2020. Removing Per‐ and Polyfluoroalkyl Substances from Groundwaters Using Activated Carbon and Ion Exchange Resin Packed Columns. *AWWA Water Science* 2(1). https://doi.org/10.1002/aws2.1172.**

Objective

This study compares PFAS removal by GAC and ion exchange resins through column studies using real drinking water sources under continuous flow conditions.

Methods

A total of eighteen columns were set up with loading rates ranging from 15-24 m/h and empty bed contact times ranging from 3.3-5.0 min. All adsorbents were obtained commercially. They are wet-crushed, sieved to achieve designed particle size, washed, and wet-packed into the columns. A constant diffusivity was used as the PFAS compounds are weakly polar, at low molecular weight, and at trace concentrations where no competition for sorption sites would occur. Dimensionless analysis was conducted to account for hydraulics and pollutant mass diffusion.

Main findings

The study found that coal-based GAC had higher adsorption capacity compared to coconut shell-based GAC, which was attributed to higher mesopore and macropore volumes. The study also found that perfluorosulfonic acids broke through later than perfluorocarboxylic acids; within the same sulfonic acid or carboxylic acid class, longer-chain PFAS broke through later than shorter-chain PFAS, due to higher hydrophobicity and molecular weight.

Limitations

The study investigated PFAS removal from the groundwater matrix, the removal goal and background composition of which were different from those of the stormwater matrix.

Relevance

The study compared the removal of different PFAS compounds with different functional groups and chain lengths by different media components through sorption and ion exchange. The study evaluated the performance of the column based on the total amount of PFAS removed.

It appears that data consistently show perfluorosulfonic acids broke through later than perfluorocarboxylic acids and long-chain PFAS broke through later than short-chain PFAS.

4. **D. Zhou, M. L. Brusseau, Y. Zhang, S. Li, W. Wei, H. Sun, C. Zheng. 2021. Simulating PFAS Adsorption Kinetics, Adsorption Isotherms, and Nonideal Transport in Saturated Soil with Tempered One-Sided Stable Density (TOSD) Based Models. *Journal of Hazardous Materials* 411: 125169. https://doi.org/10.1016/j.jhazmat.2021.125169.**

Objective

This study aims to quantify PFAS adsorption kinetics, adsorption isotherms, and nonideal transport in saturated geomedia through the TOSD model using published literature data.

Methods

This study uses the TOSD function approach for describing PFAS adsorption isotherm, PFAS adsorption rate, and PFAS transport where relatively new fractional-derivative equations were adopted.

Main findings

For the adsorption isotherm model, the TOSD-based isotherm model exhibits a similar formation to the Freundlich isotherm model but is more general and accordingly more parameters. Through kinetics and transport modeling, the study found PFAS adsorption kinetics and nonideal transport are non-equilibrium processes.

Limitations

This work takes the approach of using a one-sided stable density function, which is based on limited datasets available. In addition, it does not incorporate any characteristics of media into the modeling.

Relevance

The study offers a nice summary for the modeling of PFAS sorption to geomedia from the aspects of isotherm, kinetics, to transport.

5. **G. Niarchos, L. Ahrens, D. B. Kleja, F. Fagerlund. 2022. Per- and Polyfluoroalkyl Substance (PFAS) Retention by Colloidal Activated Carbon (CAC) Using Dynamic Column Experiments. *Environmental Pollution* 308: 119667. https://doi.org/10.1016/j.envpol.2022.119667.**

Objective

The objective of this study is to investigate the effectiveness of adding colloidal activated carbon on retaining PFAS compounds in soils.

Methods

A total of 10 perfluoroalkyl acids (PFAAs) with different chain lengths (C5–C11 perfluoroalkyl carboxylic acids (PFCAs) and C4, C6, C8 perfluoroalkane sulfonates (PFSAs)) and two alternative PFAS 6:2 and 8:2

fluorotelomer sulfonates were assessed. Soil columns were set up with and without 0.03% w/w of activated carbon amendment.

Main findings

Results showed high retardation rates for long-chain PFAS and eight times higher retardation in the CAC-treated soil compared to the non-treated reference soil for the PFAS. Replacement of shorter chain perfluorocarboxylic acids (PFCAs) by longer chained PFAS was observed, indicating competition effects exist between PFAS compounds. Mass balance calculations showed 37% retention of PFAS in treated soil columns after completion of the experiments, which is 99.7% higher than the reference soil. Redistribution and elution of CAC were detected using organic carbon analysis.

Limitations

The study focuses on a specific medium, i.e., CAC, and its effectiveness in removing different PFAS compounds. The difference between the properties of CAC-treated and non-treated soils was not discussed.

Relevance

The study consistently supports the idea that long-chain PFAS compounds are easier to retain than short-chain PFAS compounds.

6. **J. C. Pritchard, K. M. Hawkins, Y.-M. Cho, S. Spahr, S. D. Struck, C. P. Higgins, R. G. Luthy. 2023. Black Carbon-Amended Engineered Media Filters for Improved Treatment of Stormwater Runoff. *ACS Environmental Au* 3(1): 34-46. https://doi.org/10.1021/acsenvironau.2c00037.**

Objective

The objective of this study is to assess six engineered media mixtures for removing a suite of co-contaminants comprising five metals, three herbicides, four pesticides, a corrosion inhibitor, six PFASs, five polychlorinated biphenyls (PCBs), and six polycyclic aromatic hydrocarbons (PAHs).

Methods

Six engineered media mixtures consisted of sand, zeolite, high-temperature gasification biochar, and regenerated activated carbon. Multiple sample ports were installed along the depth of the column.

Main findings

Biochar- and RAC-amended engineered media filters removed nearly all of the TrOCs in the effluent over the course of three months of continuous flow (480 empty bed volumes). Biochar provided greater benefits to trace organic contaminant removal than RAC on a mass basis. This study provides proof-of-concept for biochar- and RAC-amended engineered media filters operated at a flow rate of 20 cm hr−1 for removing dissolved trace organic contaminants and metals.

Limitations

The physicochemical properties of each media were not well characterized. The study presents the effectiveness of columns for individual pollutants; however, it is difficult to estimate the overall performance of the columns on the pollutants overall.

Relevance

The study presented a recipe for producing synthetic stormwater using catch basin material and straw-derived organic carbon. Higher flow conditions (20 cm hr−1), larger-sized media (0.42−1.68 mm), and downflow configuration with outlet control were used in this study to better represent field conditions.

7. **B. A. Parker, C. A. Kanalos, T. S. Radniecki, S. L. Massey Simonich, J. A. Field. 2023. Evaluation of Sorbents and Matrix Effects for Treating Heavy Metals and Per- And Polyfluoroalkyl Substances as Co-Contaminants in Stormwater. *Environmental Science: Water Research & Technology*. https://doi.org/10.1039/D3EW00028A.**

Objective

The objective of this study is to compare sorbents for the removal of heavy metals (copper and zinc) and PFAS, including perfluoroalkyl carboxylates and perfluoroalkyl sulfonates, from stormwater to inform sorbent selection for use at a field demonstration site. In addition, the major components of stormwater were characterized to evaluate their impact on sorbent performance.

Methods

Four sorbents, including two biochars produced from Douglas fir or hazelnuts, a GAC used in impacted DoD sites, and another GAC known to possess net positive charges, were characterized for cation exchange capacity, pH, and organic carbon (loss on ignition method). The four sorbents were first tested in simple synthetic stormwater in a batch system. Sorbents selected were then tested with field-collected stormwater. The best performing sorbent was then tested for the effect of salts, iron, and organic matter.

Main findings

The study concluded that a series of sorbents with different physical properties are necessary for the removal of both heavy metals and PFAS. Biochar Basic and RemBind were selected for the removal of heavy metals and PFAS, respectively, due to negative and positive surface charge, respectively. Organic matter had a significant impact on PFAS removal by RemBind.

Limitations

The relationship between the properties of sorbents and their effectiveness was qualitative, partly due to the effectiveness being evaluated based on removal percentage.

Relevance

The study used stormwater collected from two field sites, one from a site for institutional use and another from a Navy site, for part of experiments to better represent field conditions. The study provides information on how stormwater constituents affect the co-treatment of heavy metals and PFAS by sorbents.

Media Properties and Column Operations

1. **M. Gray, M. G. Johnson, M. I. Dragila, M. Kleber. 2014. Water Uptake in Biochars: The role of Porosity and Hydrophobicity. *Biomass and Bioenergy* 61: 196-205. https://doi.org/10.1016/j.biombioe.2013.12.010.**

Objective

The objective of this study is to determine how porosity and hydrophobicity interact to control total water uptake by biochar. Four hypotheses were taken: (1) biochars produced from different feedstocks would exhibit different water uptake characteristics and (2) water uptake would vary as a function of pyrolysis temperature within each feedstock. (3) the comparison between ethanol and water uptakes will allow assessment of the relative importance of hydrophobicity versus total porosity. (4) biochars exposed to air saturated with moisture would take up more water than biochars kept at ambient relative humidity.

Methods

Thorough physical and surface chemical characterization was conducted, including carbon analysis, BET surface area, density, FTIR, etc. The uptake of ethanol was compared to that of water to distinguish porosity effects from surface chemistry effects.

Main findings

The results indicate that feedstock controls residual microporosity, whereas production temperature controls hydrophobicity and pyrogenic nanopore formation. The total porosity is composed primarily of external pores and residual macropores. However, pyrogenic nanopores provide the majority of biochar surface area critical to contaminant and nutrient sorption.

Limitations

N/A

Relevance

The method for quantifying the hydrophobicity of biochar, along with methods for various surface properties, can be adopted in the current project.

2. **R. A. Tirpak, A. N. Afrooz, R. J. Winston, R. Valenca, K. Schiff, S. K. Mohanty. 2021. Conventional and Amended Bioretention Soil Media for Targeted Pollutant Treatment: A Critical Review to Guide the State of the Practice. *Water Research* 189: 116648. https://doi.org/10.1016/j.watres.2020.116648.**

Objective

Alternative engineered amendments have been tested to supplement bioretention soil media commonly consisted of sand, sandy loam, loamy sand or topsoil amended with compost. The objective of this review is to provide clear guidance on how to select the right amendment to treat a target stormwater contaminant under highly variable climatic conditions.

Methods

The review provides the guidance on engineered media selection by (1) summarizing the current design BSM specifications adopted by jurisdictions worldwide, (2) comparing the performance of conventional and amended BSM, (3) highlighting advantages and limitations of BSM amendments, and (4) identifying challenges for implementing amendments in field conditions.

Main findings

BSM specifications vary substantially between jurisdictions and pollutant removal in BSM varies by orders of magnitude. BSM amendments, including biochar, peat moss, coconut coir, iron-based amendments, fly ash, and zeolite, are effective at providing notable improvements. The performance of these amendments on pollutant removal is dependent on removal processes and pollutant type.

Existing laboratory studies on BSM are difficult to compare due to the lack of control BSM. Further, translation of laboratory scale research to field scale is challenging. It was recommended that regulatory agencies should develop BSM specifications that allow designers and engineers the flexibility to include approved amendments in media mixtures based on target pollutants.

Limitations

N/A

Relevance

The review summarizes bioretention soil mixes from selected jurisdictions, and the removal mechanisms and corresponding properties of BSM that can induce the removal mechanisms.

APPENDIX B. PRESENTATION ON OPENHYDROQUAL

Appendix B

BMP Mechanisms and Processes for Pollutant Treatment

Model Selection & Development

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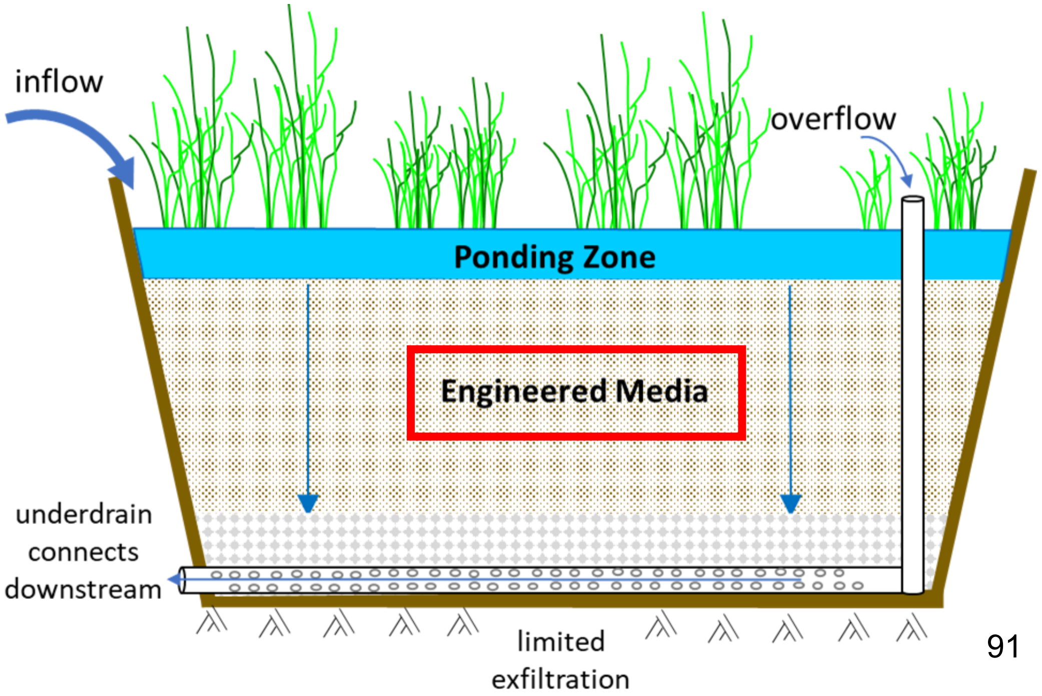
February 4, 2025

Background

- BMP treatment is represented in typically modeled as %-removal (black box for “treatment”)
- Measured performance often doesn’t match assumed %-removals



Problem Statement

- Lack of process-based design leads to uncertainty and unpredictability in BMP performance.
- Uncertainty yields concern over whether receiving water quality objectives will be met when a watershed management plan is implemented.

Big Research Question –

Can we use **properties of the media** to **accurately predict pollutant treatment** in biofiltration BMPs?

Roadmap

▼

Laboratory testing > Mechanistic model > Field application

CALIFORNIA
Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

SOUTHERN CALIFORNIA
STORMWATER MONITORING
COALITION

Approach

- Key decisions to date
  - ☑ What pollutants are we targeting?
    - Informed by Literature Review
  - ☑ What property is most important?
    - Informed by Laboratory Batch Testing
  - ☑ How much treatment is predicted by media with these properties?
    - Informed by Laboratory Column Testing
  - ➡ How do we translate observed treatment in the lab to predictions of treatment in the field?
    - Informed by Desktop Modeling

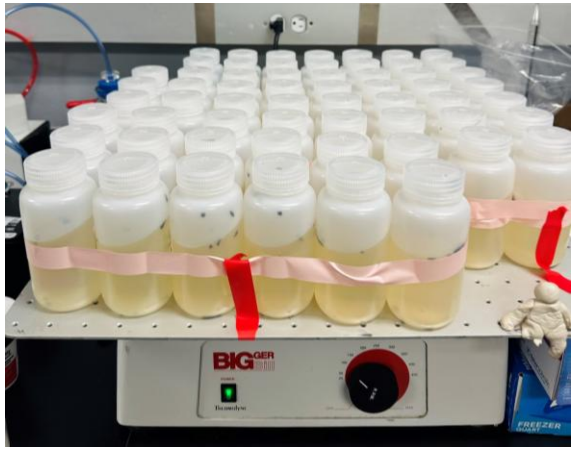
What are the Targets?

- **BMP type:** Biofiltration
  - Among most commonly constructed BMPs in SoCal
- **Target pollutants:** Dissolved Cu and PFAS (PFOA and PFOS)
  - Among least well studied
  - Dissolved metals pose greater risk to receiving environments vs particulate
- **Treatment mechanism:** Sorption
  - Can be manipulated with media characteristics
  - Sedimentation and physical filtration are well understood

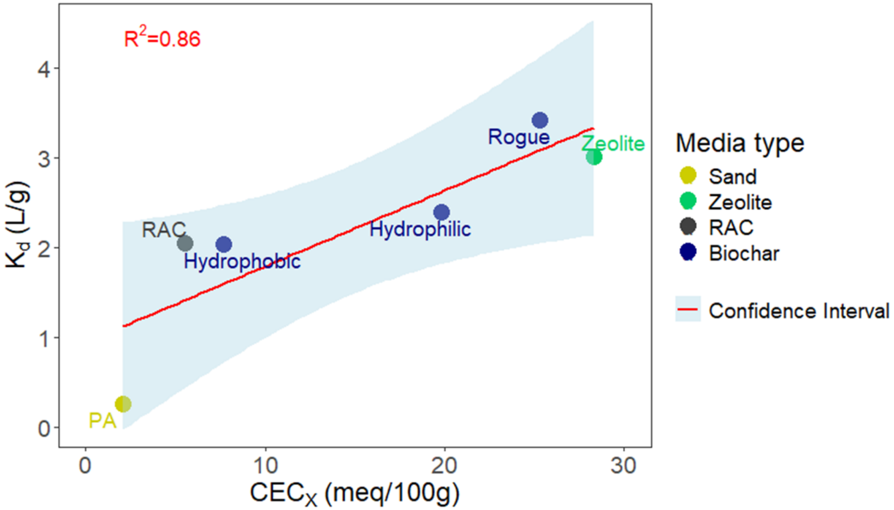
What properties should we use?

- **Cation Exchange Capacity** (CEC_X) correlated with **Partition Coefficient** (K_D)
- K_D predicts Cu sorption capacity

Candidate media characterization



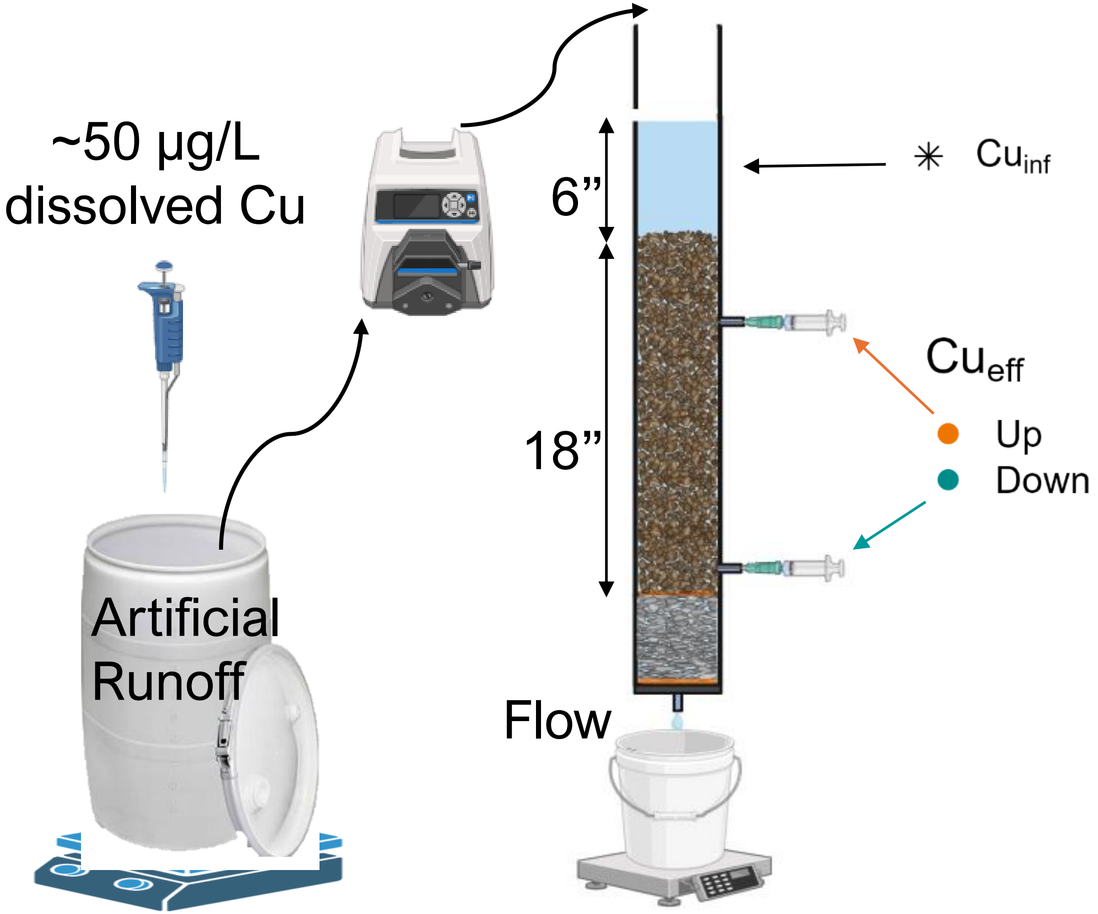
Batch sorption experiment



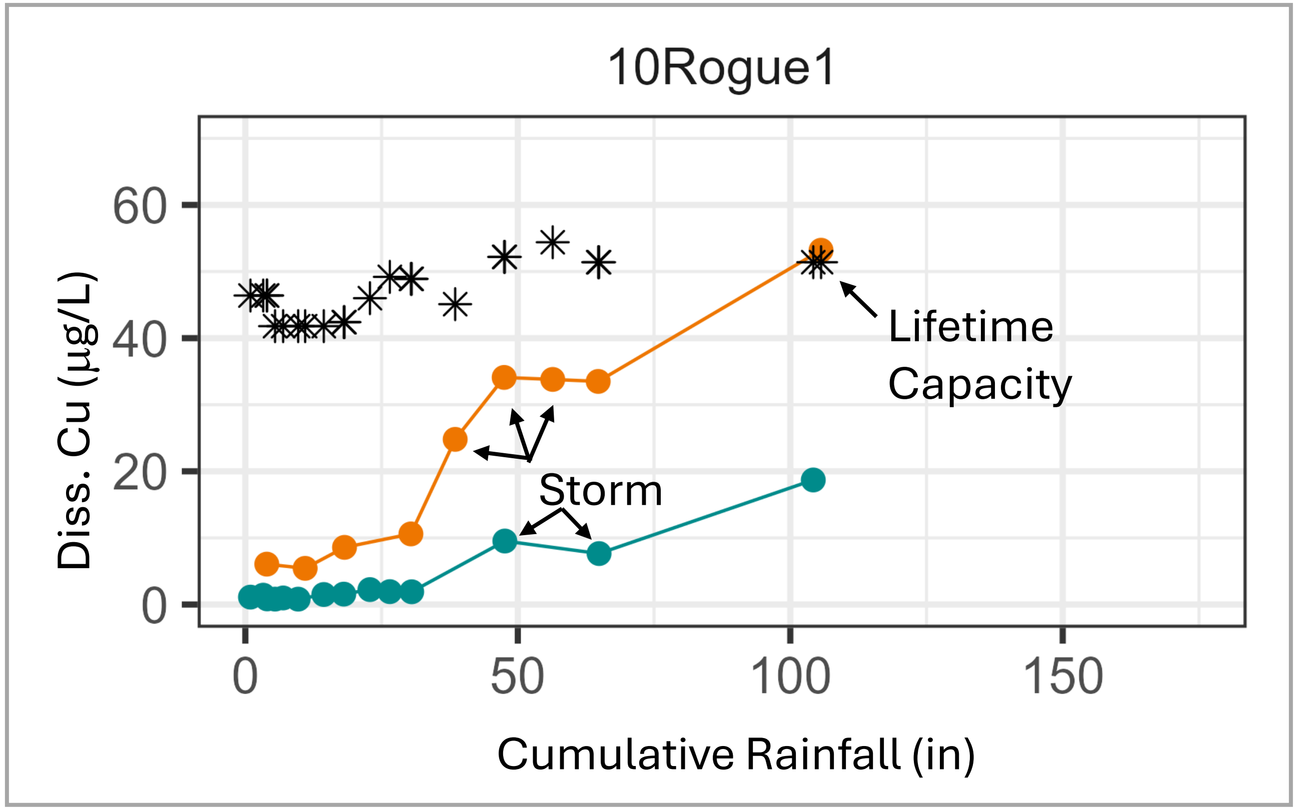
Media sorption capacity (K_D) predicted by CECx

How much treatment is predicted?

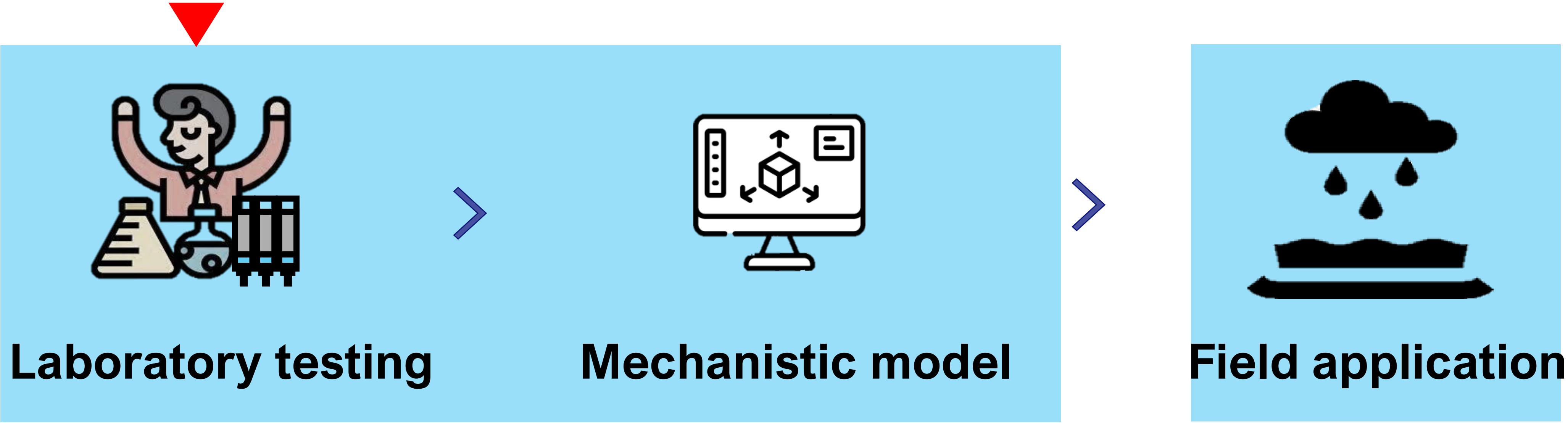
- 4 Media compositions
- 8 Individual columns



"Breakthrough Curve"



Roadmap



Laboratory testing

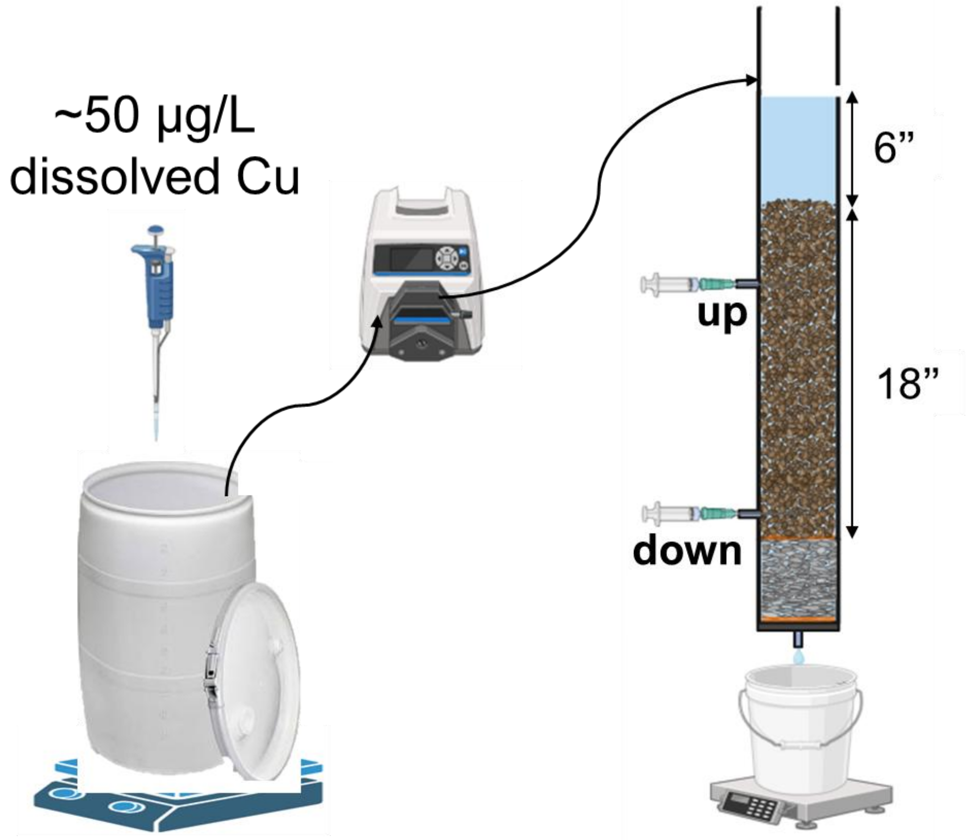
Mechanistic model

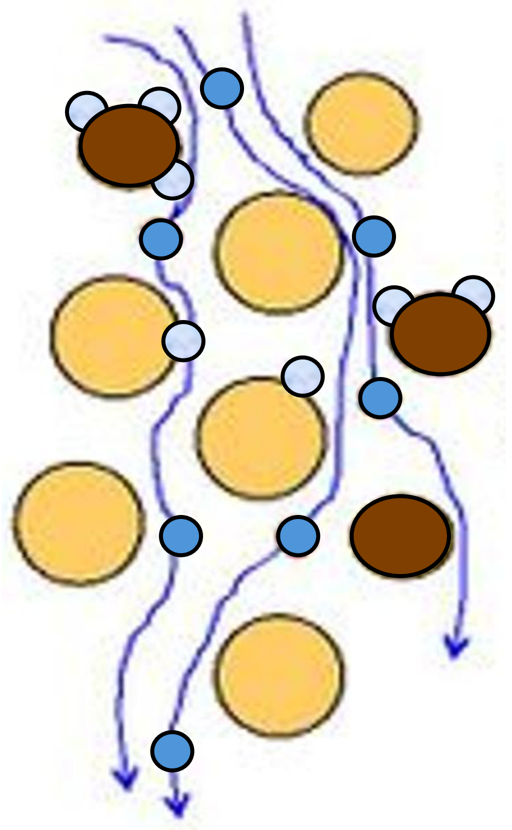
Field application

CALIFORNIA
Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

SOUTHERN CALIFORNIA
STORMWATER MONITORING
COALITION

Mechanistic Model of Column Experiment





Water Flow

● Dissolved Copper

○ Sorbed Copper

Engineered Media

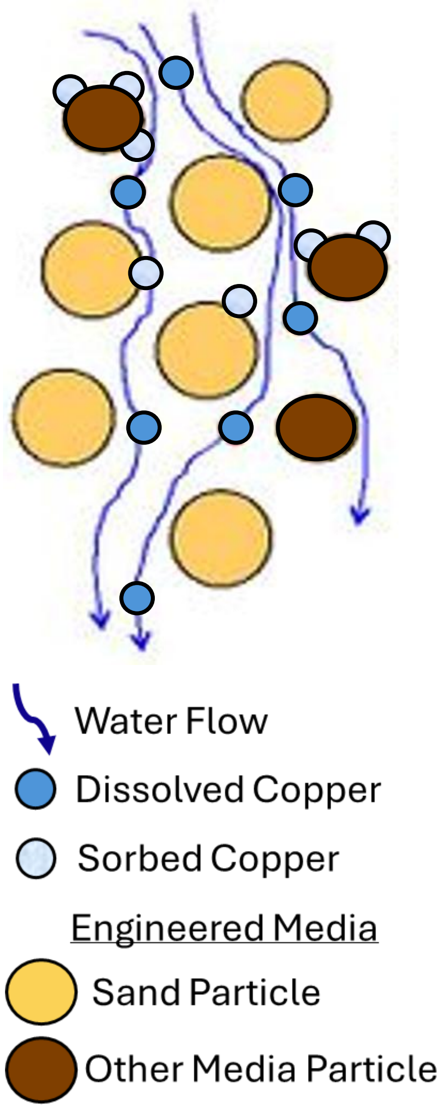
● Sand Particle

● Other Media Particle

Sorption

Advection-Dispersion-~~Reaction~~

Advection

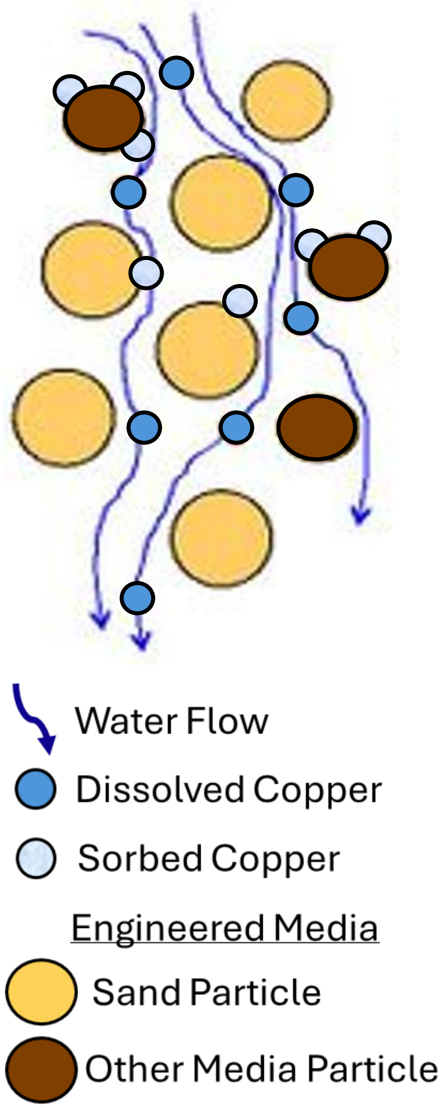


Change in concentration with time

$$\frac{\delta c}{\delta t} = -v\frac{\delta c}{\delta z}$$

How fast the coppery water is moving

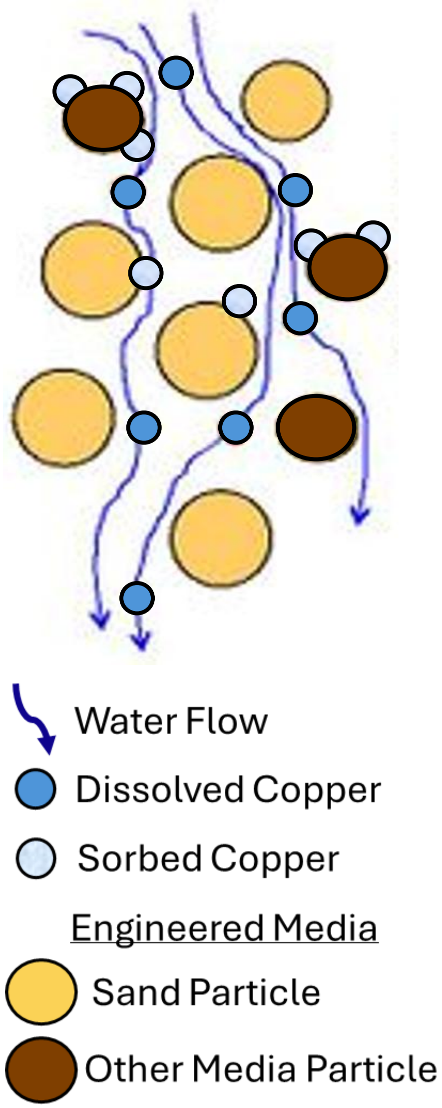
Advection – Dispersion



$$\overbrace{\frac{\delta c}{\delta t} + v\frac{\delta c}{\delta z}}^{\text{Change in Diss. Cu Conc.}} = D\frac{\delta^2 c}{\delta z^2}$$

Variable flow paths (also molecular diffusion) cause the copper to spread out

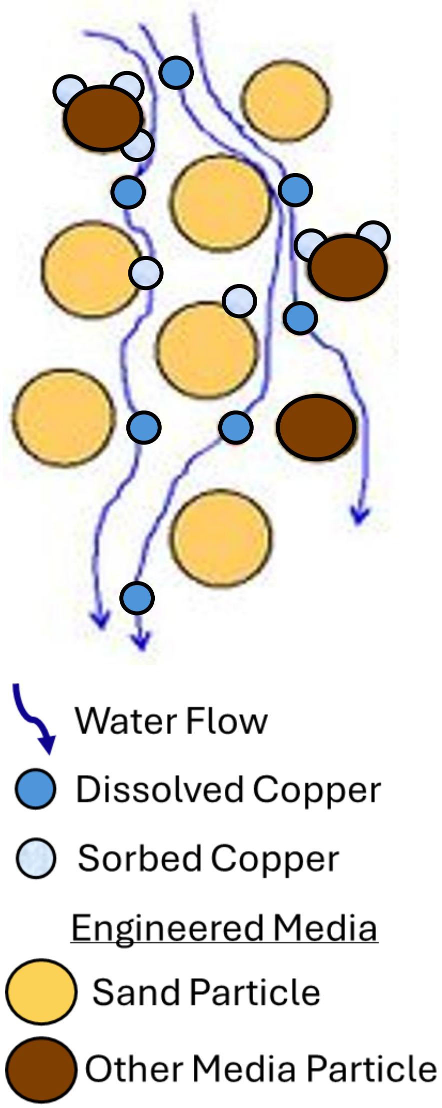
Advection – Dispersion – Sorption



$$\overbrace{\frac{\delta c}{\delta t} + v\,\frac{\delta c}{\delta z}}^{\text{Change in Diss Conc}} = \overset{\text{Dispersion}}{D}\,\frac{\delta^2 c}{\delta z^2} - \overbrace{k_f \mathrm{c}}^{\text{Entering solid phase}} + \overbrace{k_r s}^{\text{Leaving solid phase}}$$

Sorption causes some of the copper to transform

Advection – Dispersion – Sorption Model

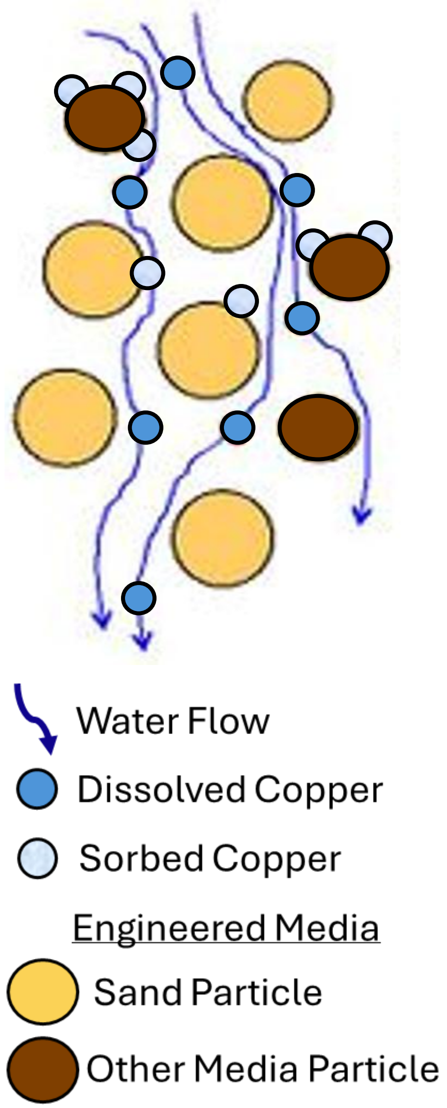


$$\overbrace{\frac{\delta c}{\delta t} + v\frac{\delta c}{\delta z}}^{\text{Change in Aqueous Conc}} = \overset{\text{Dispersion coeff}}{D}\,\frac{\delta^2 c}{\delta z^2} + \overbrace{(k_r s - k_f \mathrm{c})}^{\text{Conc diff between phases}}$$

$$\underbrace{\frac{\delta s}{\delta t}}_{\text{Change in Solid Conc}} = \underset{\text{Media Properties}}{\frac{\theta}{\rho}}\underbrace{(k_f \mathrm{c} - k_r s)}_{\text{Conc diff between phases (converse)}}$$

Two-phase Coupled PDE

Advection – Dispersion – Sorption Model



$$\overbrace{\frac{\delta c}{\delta t} + v\,\frac{\delta c}{\delta z}}^{\text{Change in Aqueous Conc}} = \overset{\substack{\text{Dispersion}\\ \text{coeff}\\ \downarrow}}{D}\,\frac{\delta^2 c}{\delta z^2} + \overbrace{(k_r s - k_f c)}^{\text{Conc diff between phases}}$$

$$\underbrace{\frac{\delta s}{\delta t}}_{\text{Change in Solid Conc}} = \underset{\substack{\uparrow\\ \text{Media}\\ \text{Properties}}}{\frac{\theta}{\rho}}\,\underbrace{(k_f c - k_r s)}_{\text{Conc diff between phases (converse)}}$$

<u>Research Question</u>: Can we use **properties of the media** to accurately predict pollutant treatment in biofiltration BMPs?

Partitioning Coefficient
(Measured in Batch test)

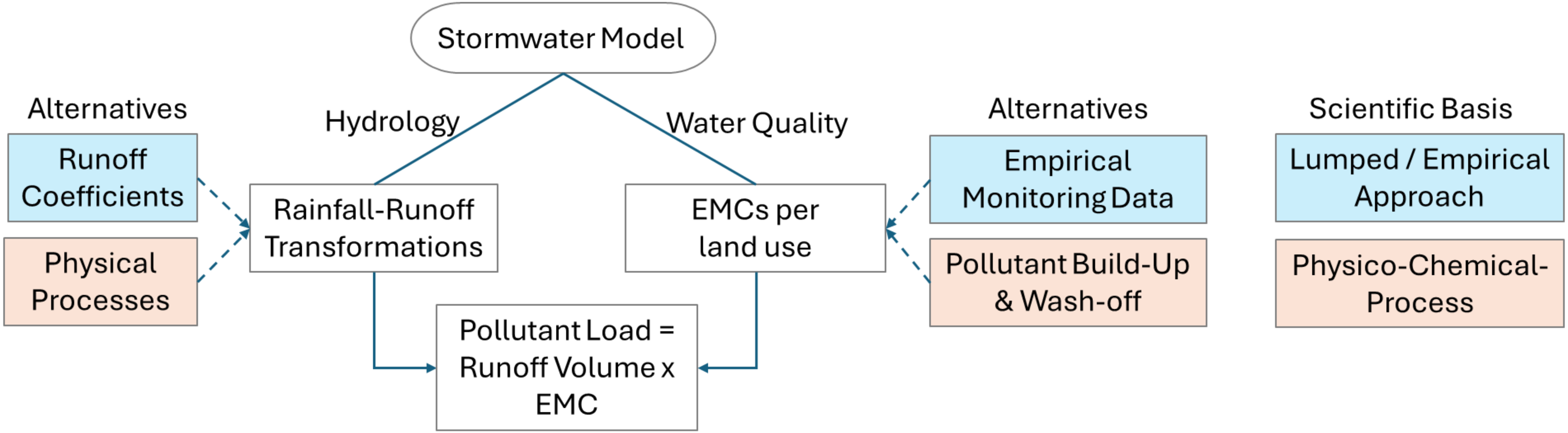
$$K_D = {k_f}/{k_r}$$

Forward rate / Reverse rate

Sorbing to solid phase

Desorbing back into solution

Stormwater Modeling Basics



Stormwater Model

Hydrology

Water Quality

Alternatives

Runoff Coefficients

Physical Processes

Rainfall-Runoff Transformations

EMCs per land use

Pollutant Load = Runoff Volume x EMC

Alternatives

Empirical Monitoring Data

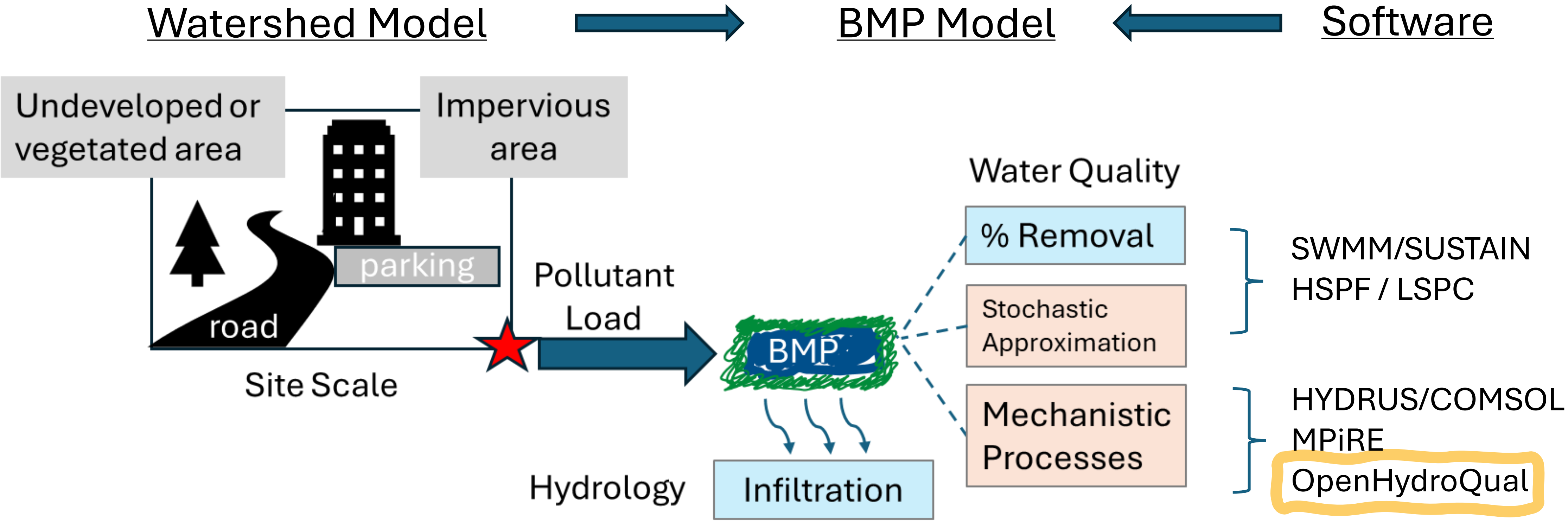
Pollutant Build-Up & Wash-off

Scientific Basis

Lumped / Empirical Approach

Physico-Chemical-Process

BMP Modeling Basics



Watershed Model → BMP Model ← Software

Undeveloped or vegetated area

Impervious area

parking

road

Site Scale

Pollutant Load

BMP

Hydrology

Infiltration

Water Quality

% Removal

Stochastic Approximation

Mechanistic Processes

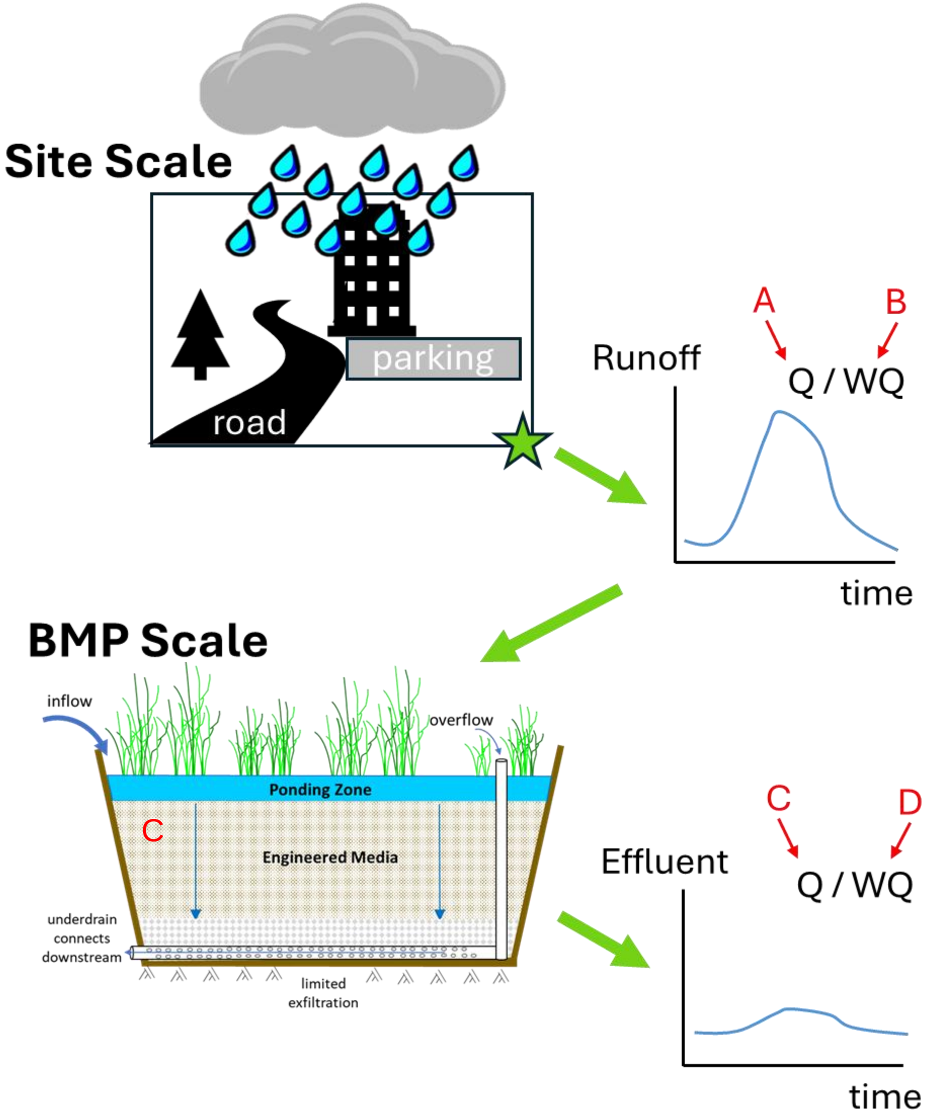
SWMM/SUSTAIN
HSPF / LSPC

HYDRUS/COMSOL
MPiRE
OpenHydroQual

OpenHydroQual

- Open source
- Fully saturated porous media flow
- User-defined reaction equations
- “Inverse-modeling” calibration
- Functional Graphical User Interface (GUI)
- Relationship w Developer
  A. Massoudieh, Catholic University of America

Field scale model→ site-scale BMPs



BMP-scale Water Quality Modeling Prerequisites:

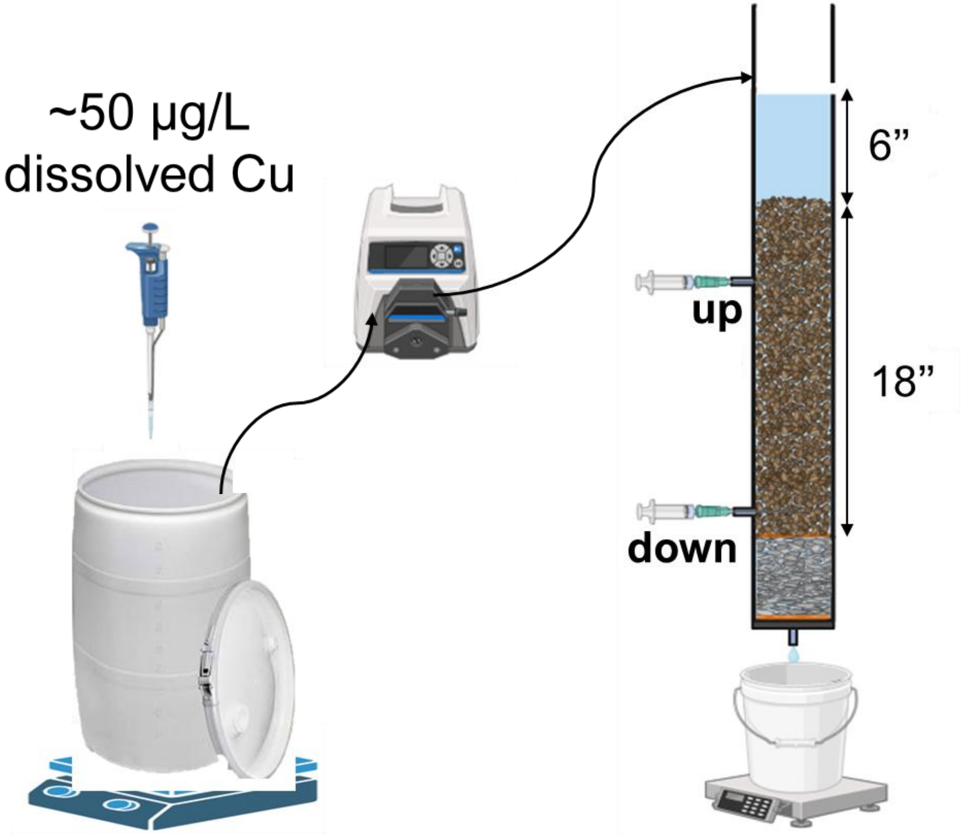
A) Decent hydrology
(Pollutants travel via water)

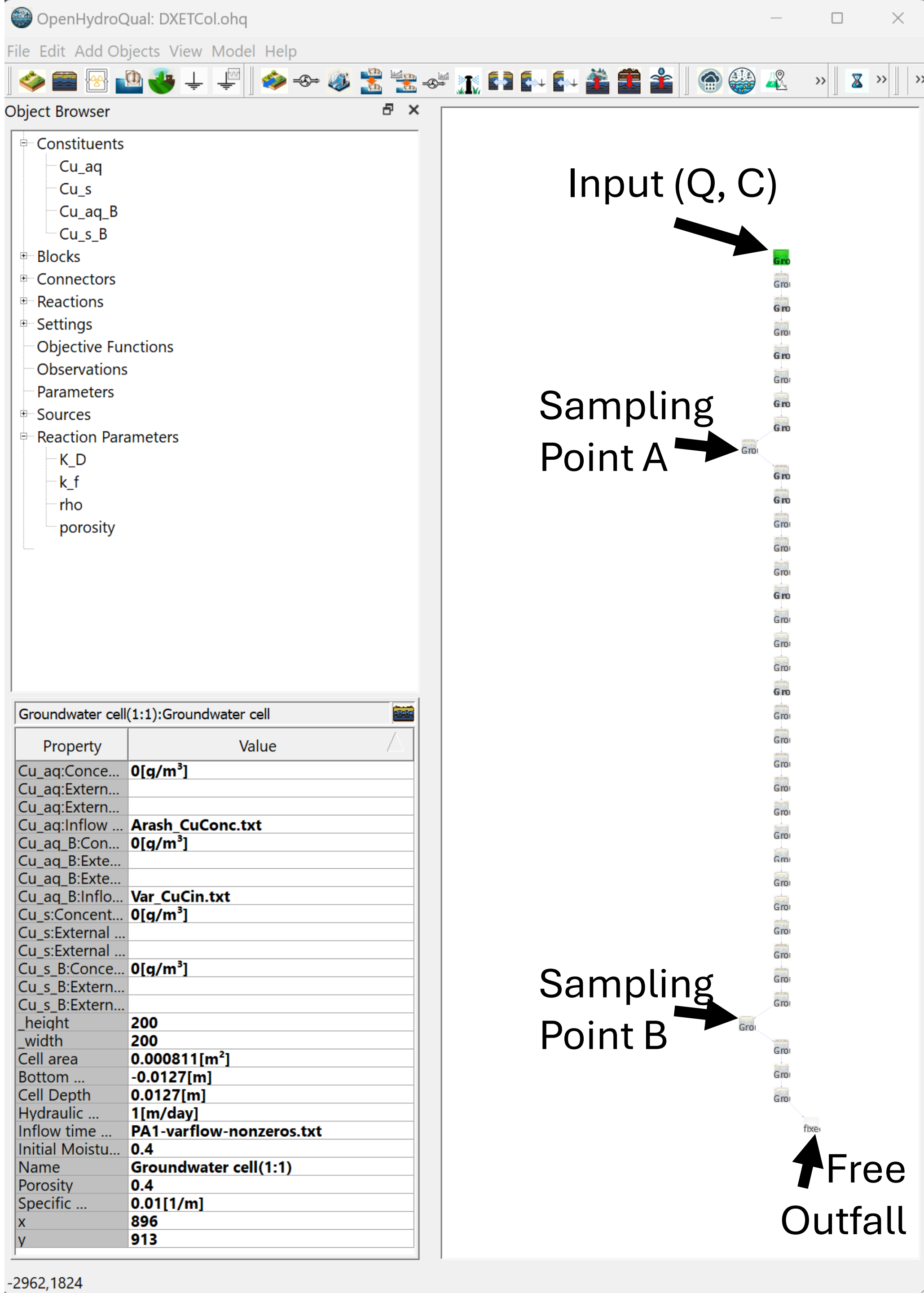
B) Accurate land use EMC data
(Surfaces generate pollutant runoff)

C) High quality BMP data
(BMP hydrology, media properties, etc.)

D) Dynamic pollutant transformations
(What is the fate of pollutants that enter the BMP?)

OpenHydroQual – Column Model Setup





Groundwater cell(1:1):Groundwater cell

Property	Value
Cu_aq:Conce...	0[g/m^3]
Cu_aq:Extern...	
Cu_aq:Extern...	
Cu_aq:Inflow ...	Arash_CuConc.txt
Cu_aq_B:Con...	0[g/m^3]
Cu_aq_B:Exte...	
Cu_aq_B:Exte...	
Cu_aq_B:Inflo...	Var_CuCin.txt
Cu_s:Concent...	0[g/m^3]
Cu_s:External ...	
Cu_s:External ...	
Cu_s_B:Conce...	0[g/m^3]
Cu_s_B:Extern...	
Cu_s_B:Extern...	
_height	200
_width	200
Cell area	0.000811[m^2]
Bottom ...	-0.0127[m]
Cell Depth	0.0127[m]
Hydraulic ...	1[m/day]
Inflow time ...	PA1-varflow-nonzeros.txt
Initial Moistu...	0.4
Name	Groundwater cell(1:1)
Porosity	0.4
Specific ...	0.01[1/m]
x	896
y	913

Advection – Dispersion – Sorption Model

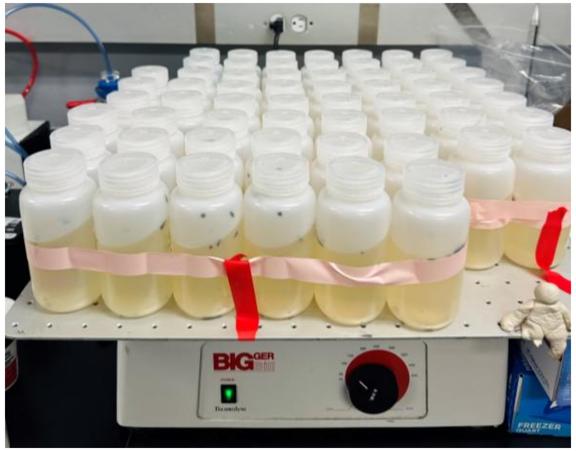
Parameters:

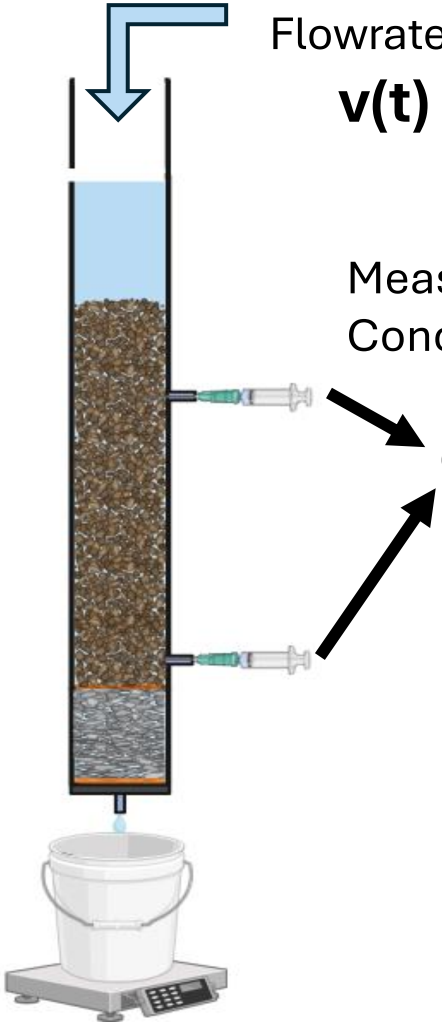
- θ ← Measured media porosity
- ρ ← Media bulk density
- K_D ← Measured in Batch Experiment
- v(t) ← Flowrate measured in Columns
- C(z, t) ← Diss Cu Conc at 2 ports over time
- k_f ← sorption kinetic rate
- D ← dispersion coefficient

Calibrate through modeling

Media Properties from Batch Testing:

K_D, θ, ρ





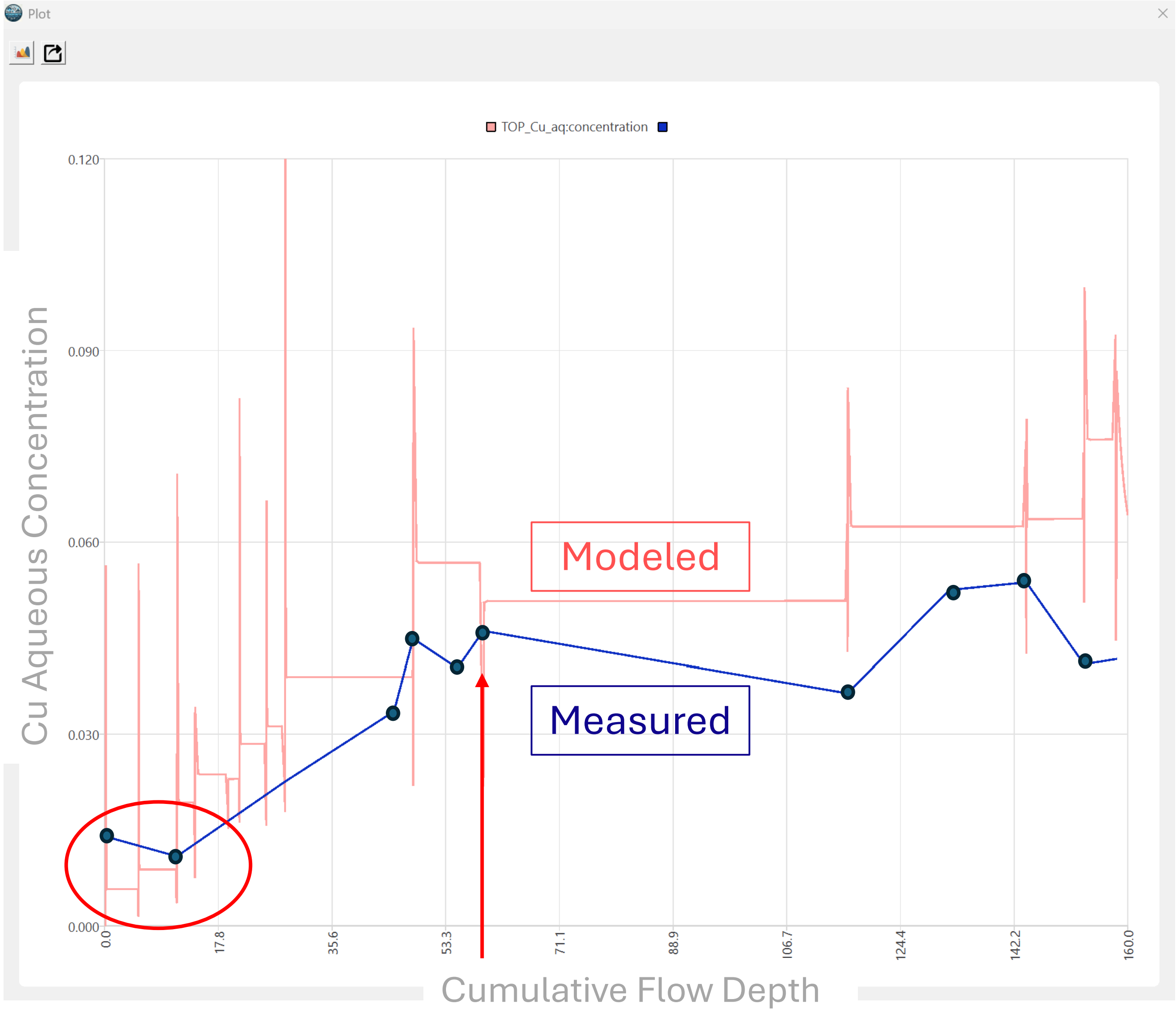
Controlled Flowrate:

v(t)

Measured Concentration

C(z,t)

OpenHydroQual – Work in Progress



“All models are wrong.
Some are useful”
- Box, 1965

Key to notice:

- Breakthrough timing
- Early effluent conc

Roadmap

Laboratory testing > **Mechanistic model** > **Field application**

CALIFORNIA
Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

SOUTHERN CALIFORNIA
STORMWATER MONITORING
COALITION

Next Steps

- Continue improving OHQ model
  - Tweaking the various nobs and levers
  - Success → K_D (measured parameter) accurately predicts treatment in columns
- Develop a Work Plan for BMP Modeling at Field Scale
  - Field BMP data collection
  - “Scale up” from columns to a “real” BMP
  - Define criteria for model success
  - Formulate modeling scenarios to inform BMP design

CALIFORNIA
Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

SOUTHERN CALIFORNIA
STORMWATER MONITORING
COALITION

Thank you! Questions?

SMC Advisory Committee Members

Robert Rodarte – Orange County PW

Rey Pellos – San Diego PW

Susana Vargas – Region 4

Matt Yeager – Riverside County FCD

Kelly Rodman – State Water Board

Michael Borst – US EPA

Jill Murray – City of Santa Barbara

SCCWRP PROJECT TEAM

Elizabeth Fassman-Beck

Danhui Xin

Edward Tiernan

Technical Advisor

Prof. Allen Davis, University of Maryland

APPENDIX C. PRESENTATION ON PILOT TESTING RESULTS

Appendix C

CALIFORNIA
Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

BMP Mechanisms and Processes for Pollutant Treatment

SCCWRP
Established 1969

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May 24, 2024

Agenda

❑ Key Outcomes

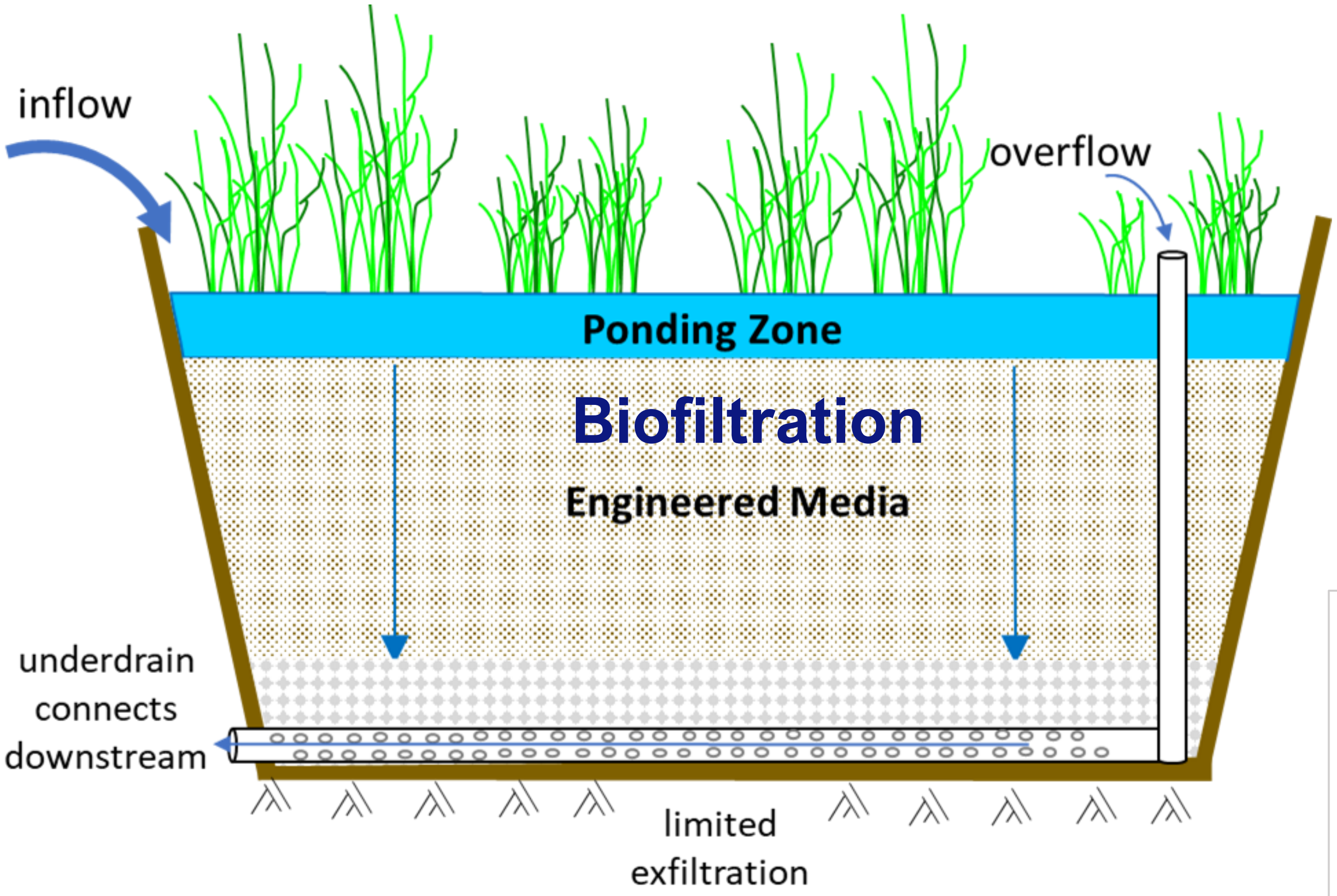
- Media CEC is a promising predictor of Cu sorption
- Pilot column experiments reached Cu breakthrough

❑ Current Activities & Next Steps

- Double column capacity and sample PFOA and PFOS

❑ Q/A

Media selection



❑ **Design specification/guidance**

- 70-90% sand
- 5-20% organic matter
- Other amendments

↓

- PA sand (ASTM C-33)
- ~~Compost~~ (eliminated due to leaching)
- Engineered materials (suitable size fractions)
  - Zeolite
  - Biochar
  - Regenerated activated carbon (RAC)

Media characterization

design guidance

mechanism: sorption

Media type	Media name	pH	Loss of Ignition	Olsen-P	NO_3^--N	CEC_{Ba}*	CEC_X	BET SA**
			weight%	mg-P/kg	mg-N/kg	meq/100g	meq/100g	m^2/g
Sand	Glass	9.12±0.02	<0.05	<20	<0.5	2.6	0.3	0.02
	PA	7.94±0.00	0.13	<1	1.52	<2	2.08	–
Commercial	85% Sand+ 15% bark	7.11±0.12	1.7	22	<0.5	4.5	3.6	1.13
Mineral	Zeolite	9.61±0.03	3.8	<20	20.0	7.6	28.3	15.16
Char	Rogue	9.58±0.04	74.6	1324	0.8	15.0	25.3	546.51
	Hydrophobic	7.75±0.07	66.4	292	2.2	13.7	7.7	237.05
	Hydrophilic	5.99±0.10	53.4	1232	20	21.0	19.8	443.62
	RAC	9.10±0.57	1.4	424	2.2	3.6	5.5	840.50

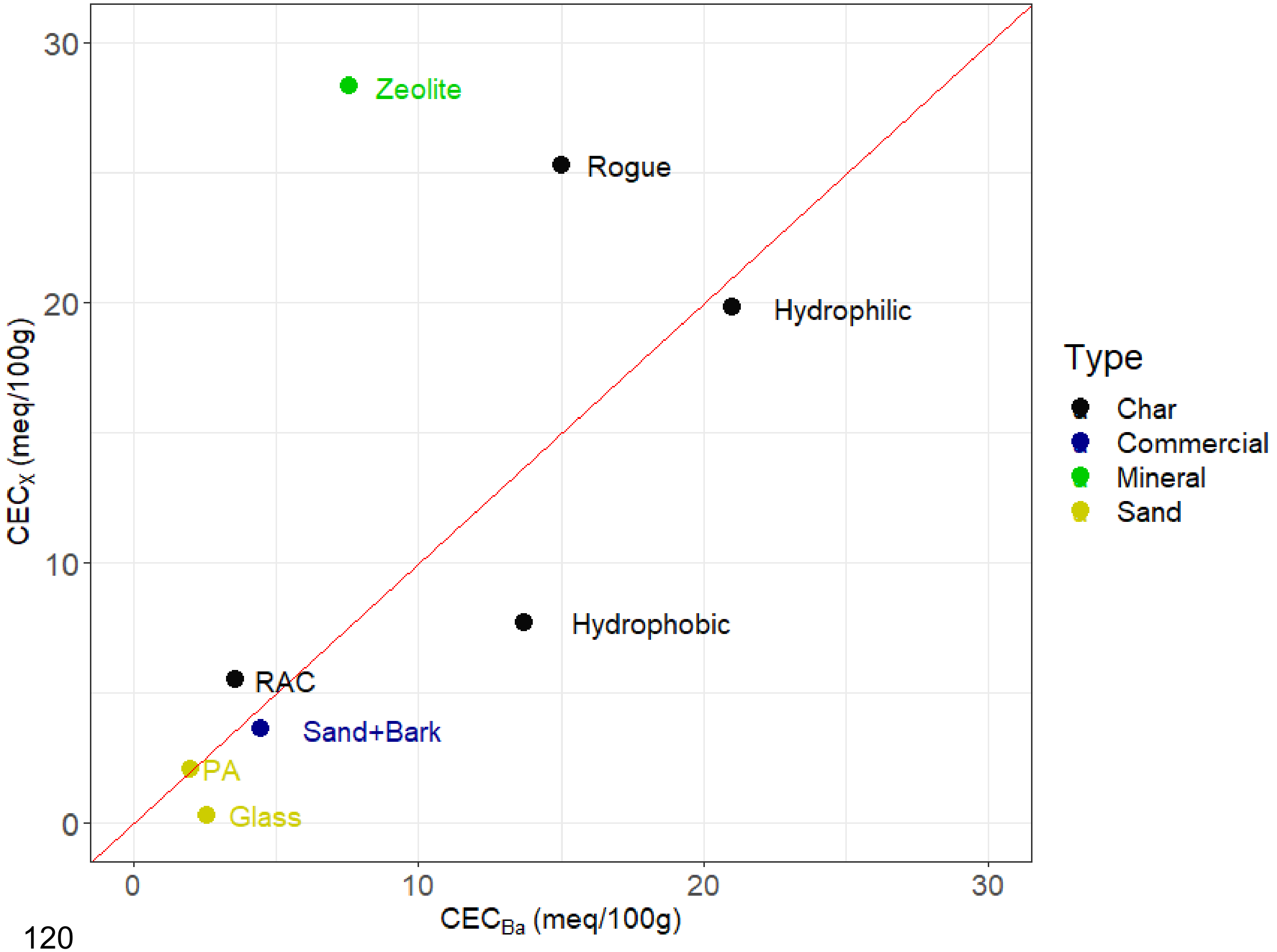
*CEC: Cation exchange capacity; **BET SA: A specific surface area

❑ Covered a broad range of properties

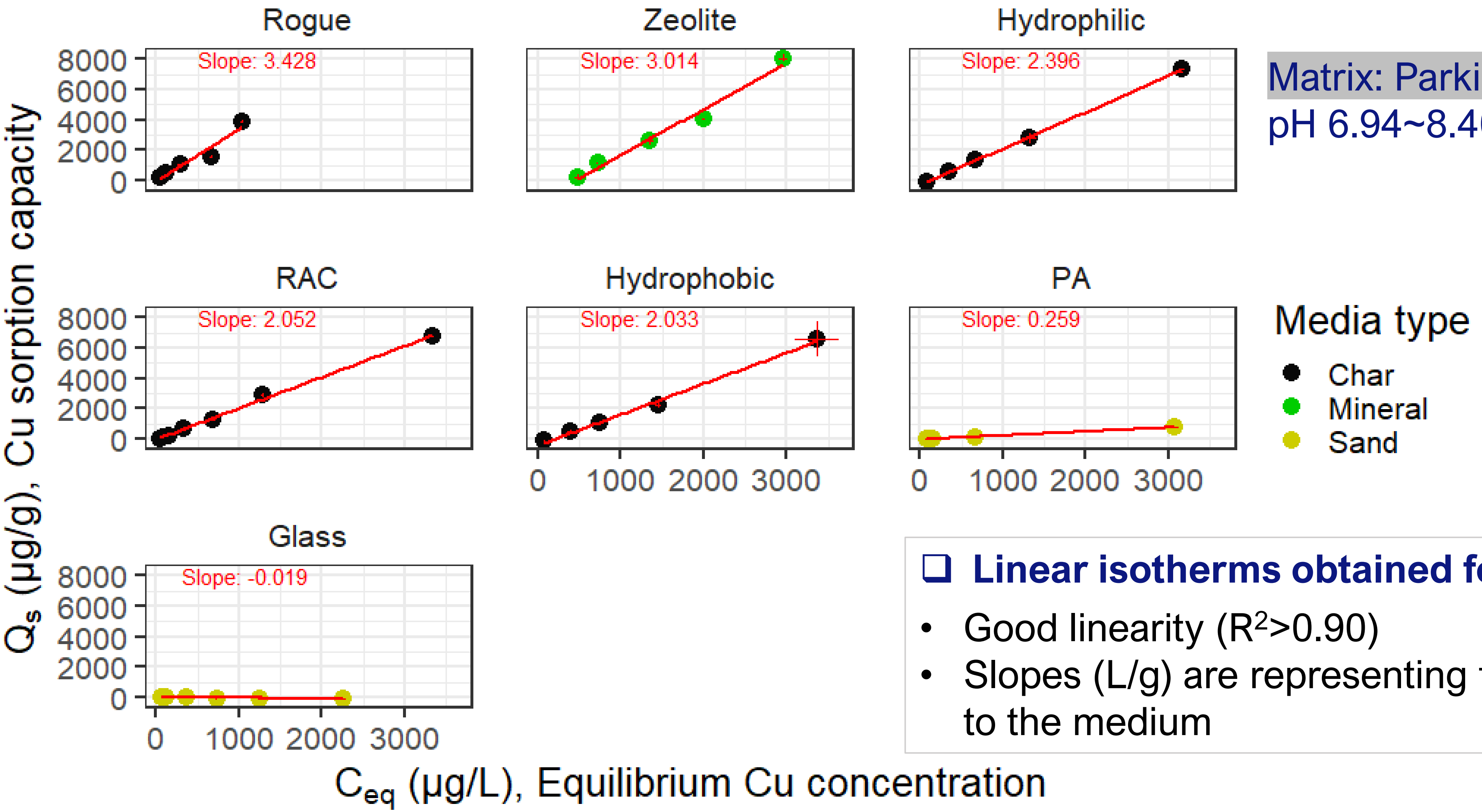
- properties — treatment mechanism – treatment effectiveness

CEC methods

- >5 different methods
- Design guidance doesn't specify the method
- We compared two common methods
    - CEC_{Ba} : Barium saturation followed by calcium replacement, quantified based on calcium loss
    - CEC_X : Ammonium saturation, quantified based on the sum of replaced K, Ca, Mg, Na



Cu sorption to media in batch reactors



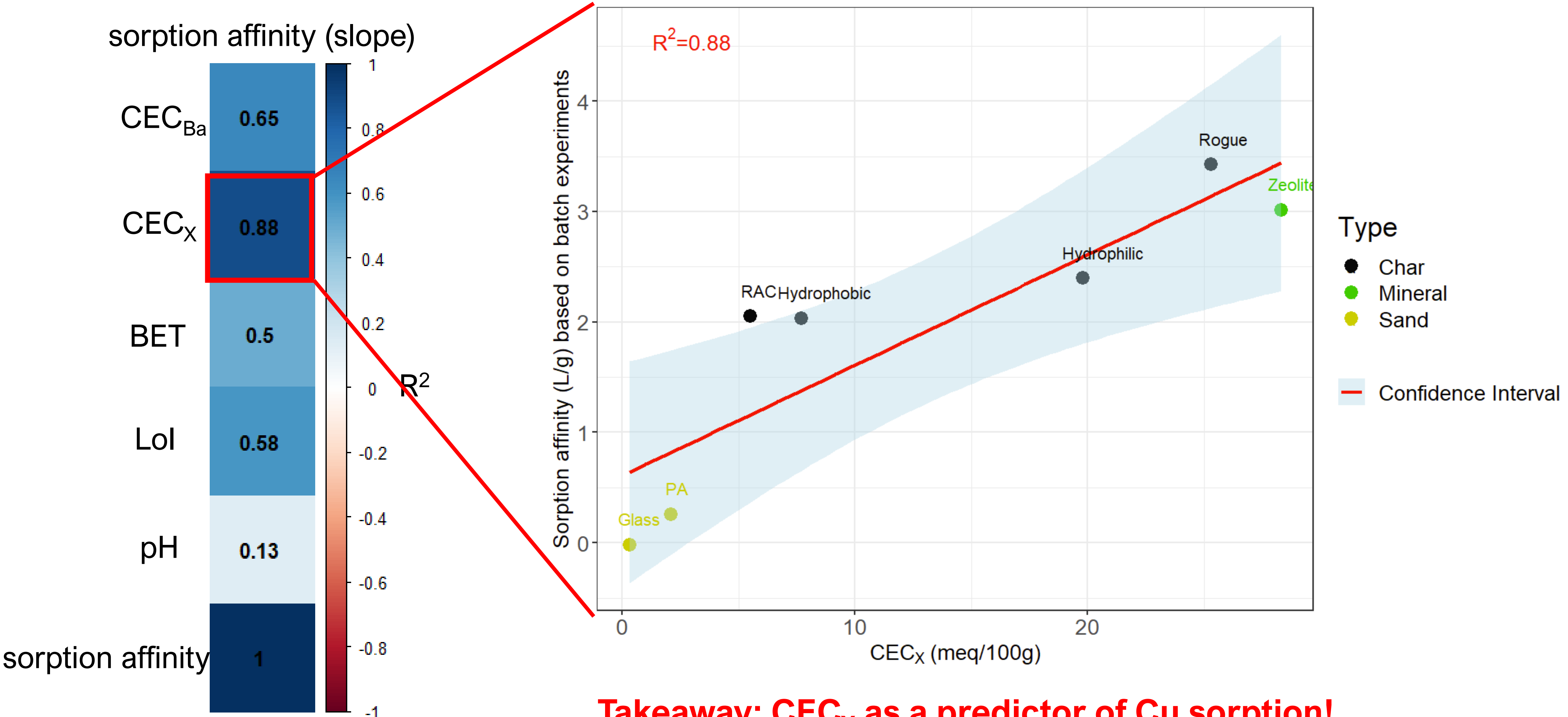
Matrix: Parking-lot runoff
pH 6.94~8.40

❑ Linear isotherms obtained for each medium

- Good linearity (R^2>0.90)
- Slopes (L/g) are representing the affinity of Cu to the medium

Media properties vs. Cu sorption

Correlation analysis



Takeaway: CEC_X as a predictor of Cu sorption!

Agenda

☐ Key Outcomes

- Media CEC is a promising predictor of Cu sorption
- Pilot column experiments reached Cu breakthrough

☐ Current Activities & Next Steps

- Double column capacity and sample PFOA and PFOS

☐ Q/A

Column setup: vertical profile mimicking biofiltration

Pilot column experiments

☐ Four columns

- 2 media compositions in duplicate
  - PA sand (PA1 and PA2)
  - PA sand with 10% of Rogue biochar by volume (10Rogue1, 10Rogue2)

☐ ~400 L of spiked runoff through each column

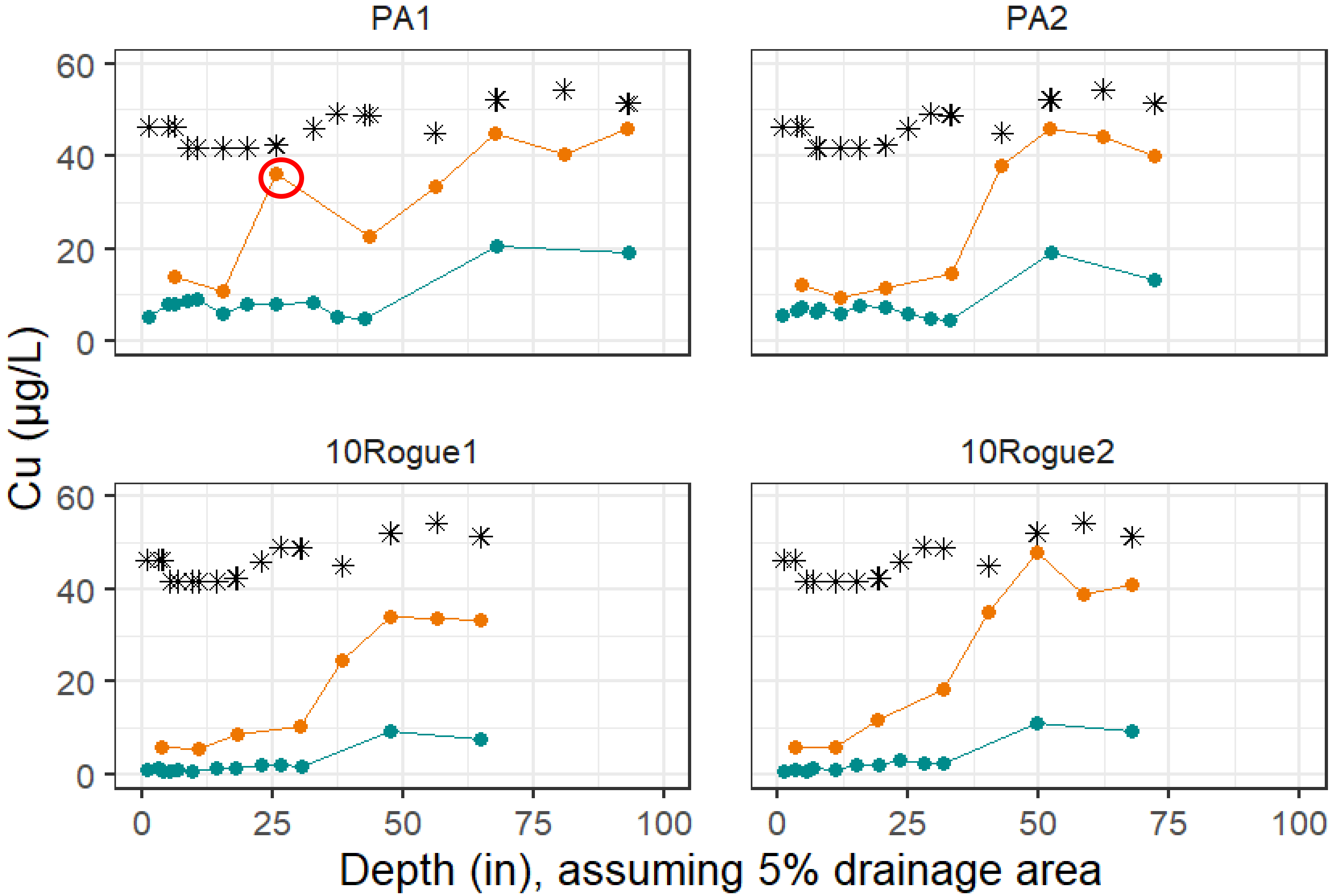
- 6-inch ponding depth
- Source: parking-lot runoff spiked with Cu^{2+}(50 µg/L), NO_3^- (1 mg/L), PFOA and PFOS (25 ng/L each) (multiple contaminants)

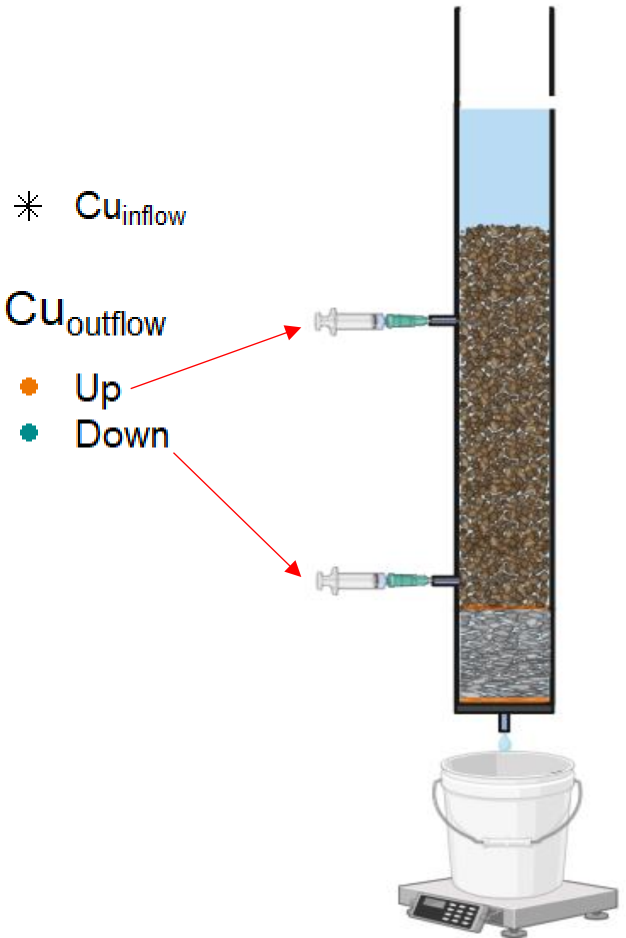
☐ Sampling

- Flow rates were monitored the whole time (30-60 in/h)
- Mainly sampling for Cu
- Up and down locations
  - **Sampling at up locations (25% depth) for early detection of breakthrough**

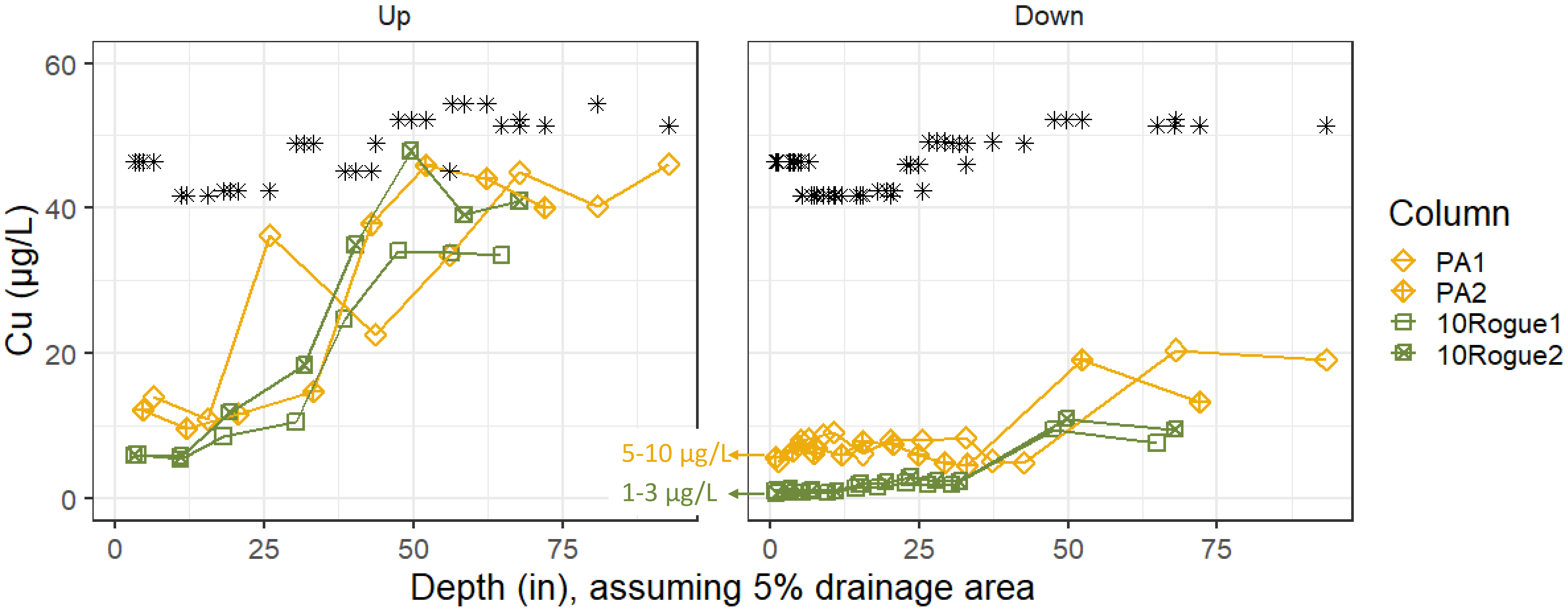
Cu breakthrough curves

- ☐ **Takeaway: Upper ports reached full breakthrough**
- 50-70 in (5-7 years)
- ☐ **Down ports started to breakthrough**





Cu breakthrough curves



- Similar trends of breakthrough curves
- Effluent concentrations: PA>10Rogue, more obvious for Down

Agenda

❑ **Key Outcomes**

- Media CEC is a promising predictor of Cu sorption
- Pilot column experiments reached Cu breakthrough

❑ **Current Activities & Next Steps**

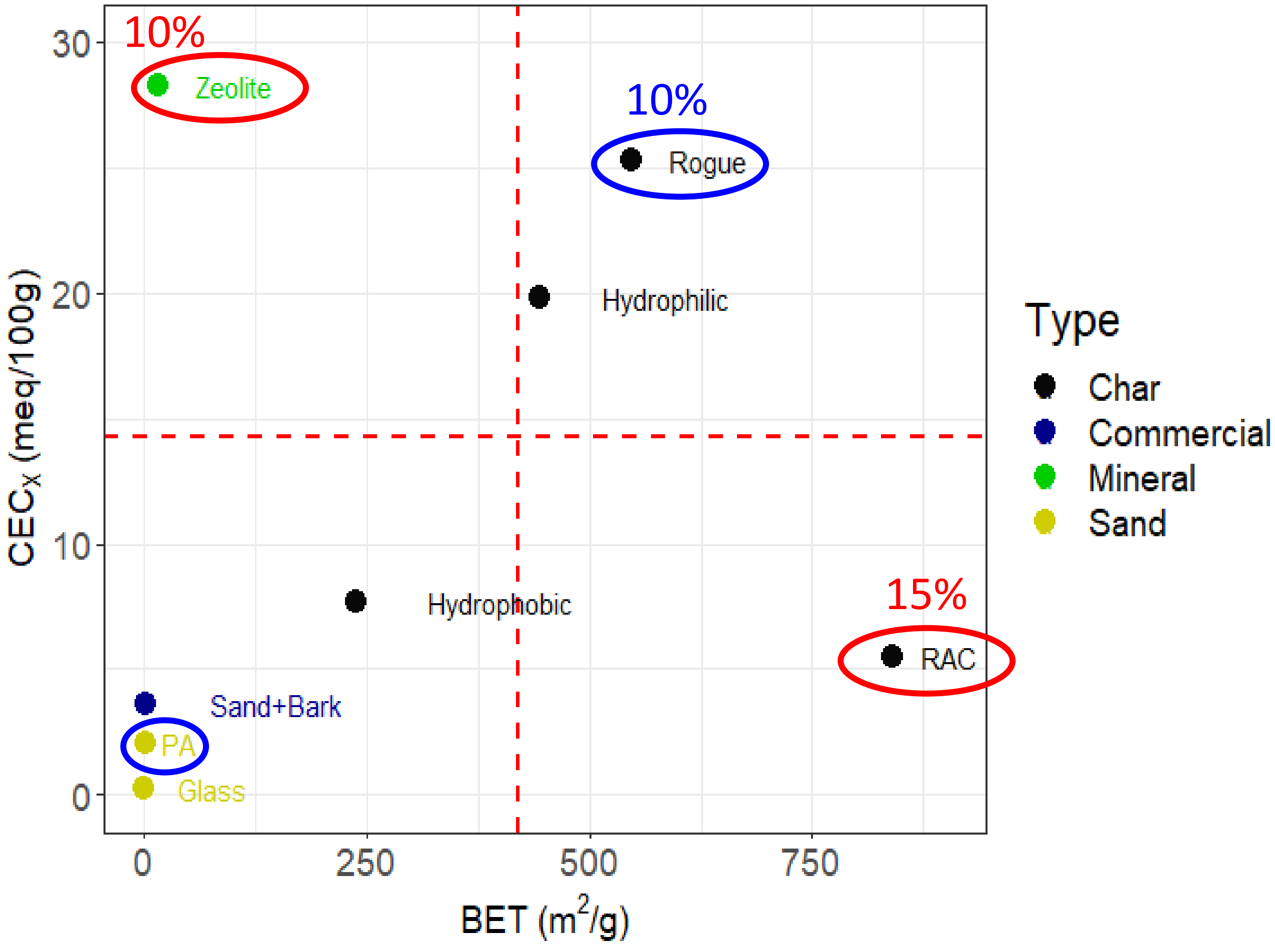
- Double column capacity and sample PFOA and PFOS

❑ **Q/A**

Current activities

❑ Double column capacity

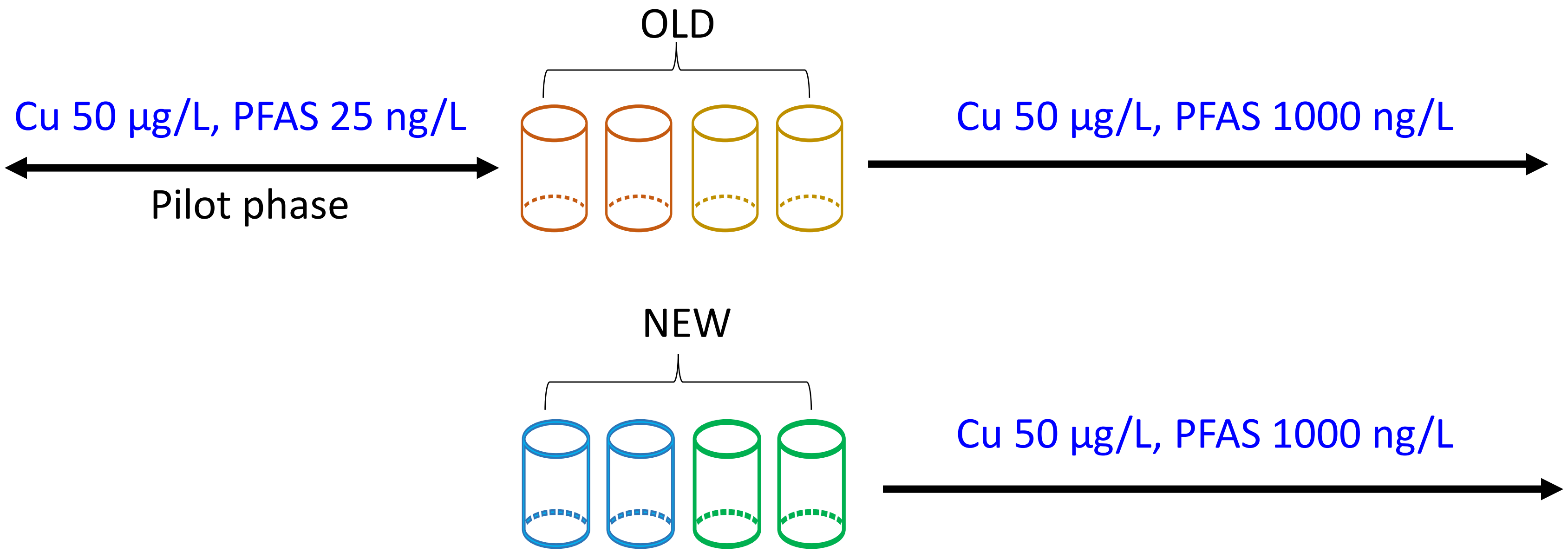
- 8 columns: 4 media compositions in duplicate



Current activities

☐ Augment PFOA and PFOS

- Continue Cu (~50 µg/L)
- PFOA and PFOS (1000 ng/L)
    - Start to sample for PFAS



OLD

Cu 50 µg/L, PFAS 25 ng/L

Pilot phase

Cu 50 µg/L, PFAS 1000 ng/L

NEW

Cu 50 µg/L, PFAS 1000 ng/L

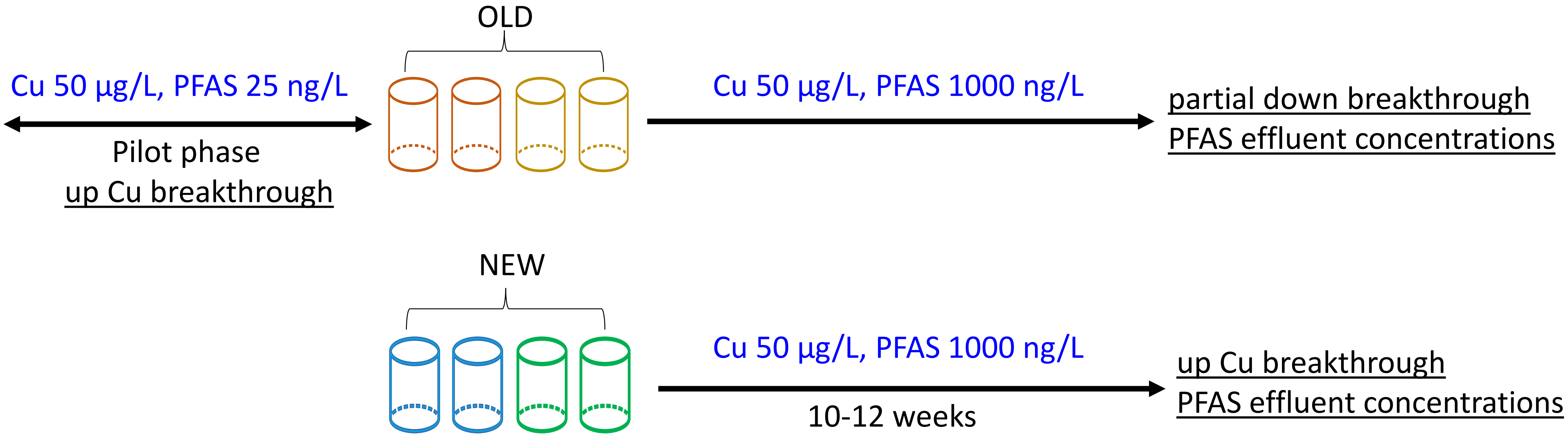
Next steps

❑ **This week: column packing & conditioning**

- Check flow rates

❑ **From next week: run columns with spiked runoff**

- For PFAS, focus on effluent concentrations
- Cu breakthroughs at Up locations for the new columns (**10-12 weeks)**



OLD

Cu 50 µg/L, PFAS 25 ng/L

Pilot phase

up Cu breakthrough

Cu 50 µg/L, PFAS 1000 ng/L

partial down breakthrough

PFAS effluent concentrations

NEW

Cu 50 µg/L, PFAS 1000 ng/L

10-12 weeks

up Cu breakthrough

PFAS effluent concentrations

Agenda

☐ **Key Outcomes**

- Media CEC is a promising predictor of Cu sorption
- Pilot column experiments reached Cu breakthrough

☐ **Current Activities & Next Steps**

- Double column capacity and sample PFOA and PFOS

☐ **Q/A**

APPENDIX D. PRESENTATION ON THE SELECTION OF CONTAMINANTS

Appendix D

Kick-off Meeting
Task 22.1

BMP Mechanisms and Processes for Pollutant Treatment

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June 30, 2023

Outline

1. Overview of project goals & timeline

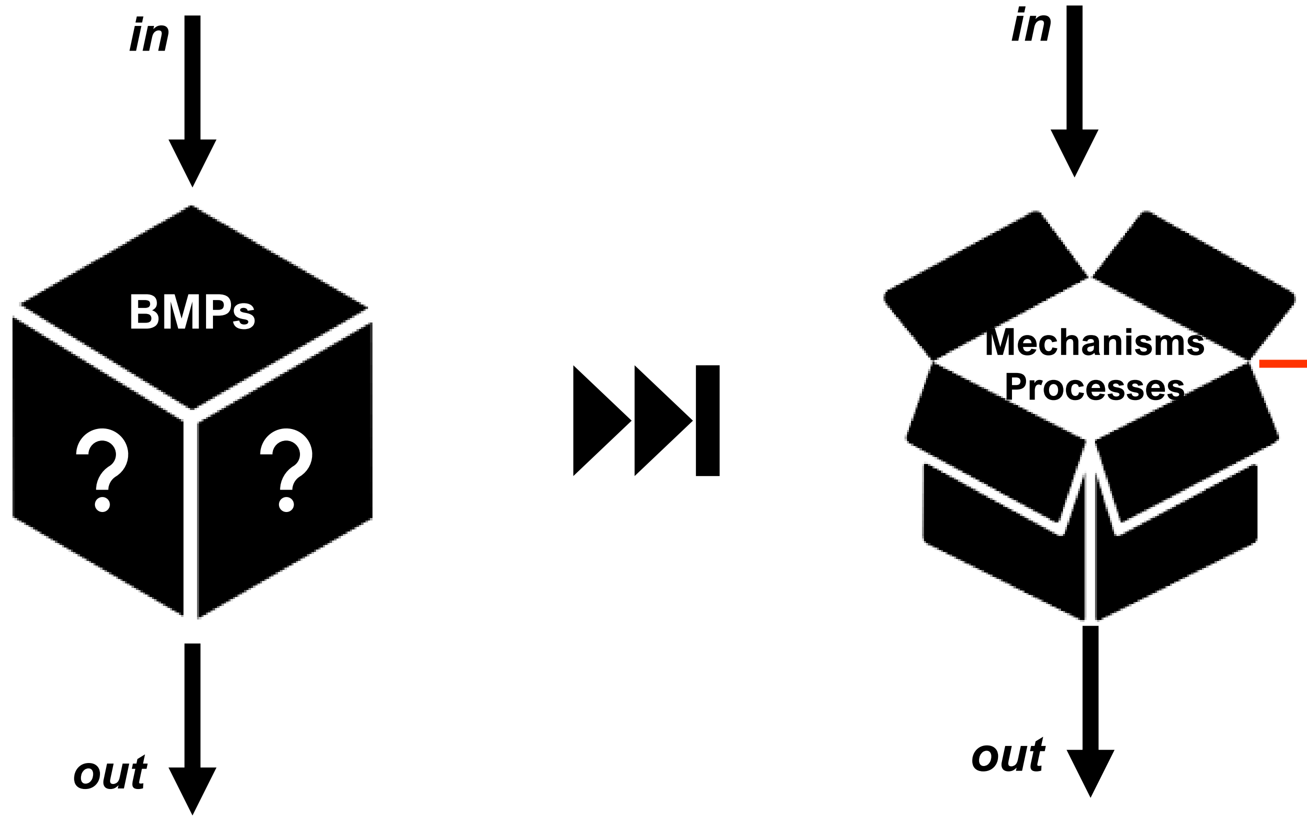
2. On the first deliverable: BMP and pollutants

3. Overall approach

4. Expected outcomes and potential challenges

5. Look ahead: pilot testing

Goal: Open the "black box"

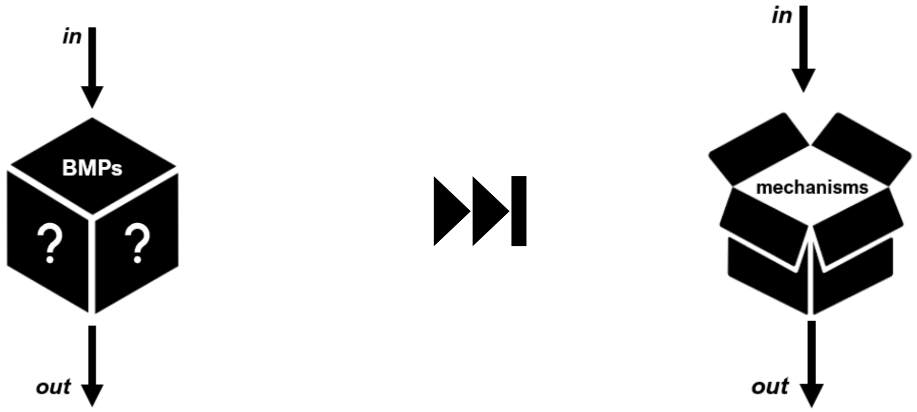


- Sedimentation
- Sorption
- Ion exchange
- Oxidation/reduction
- Biodegradation

…

We aim to identify and **quantify** the treatment **mechanisms and processes** for removing different **pollutants** from stormwater within a structural BMP.

Why care?



- Experience-based design
- Unpredictable performance

- **Process-based design**
- **Predictable performance**

BMP Engineers

Design treatment procedures that match pollutant removal goals

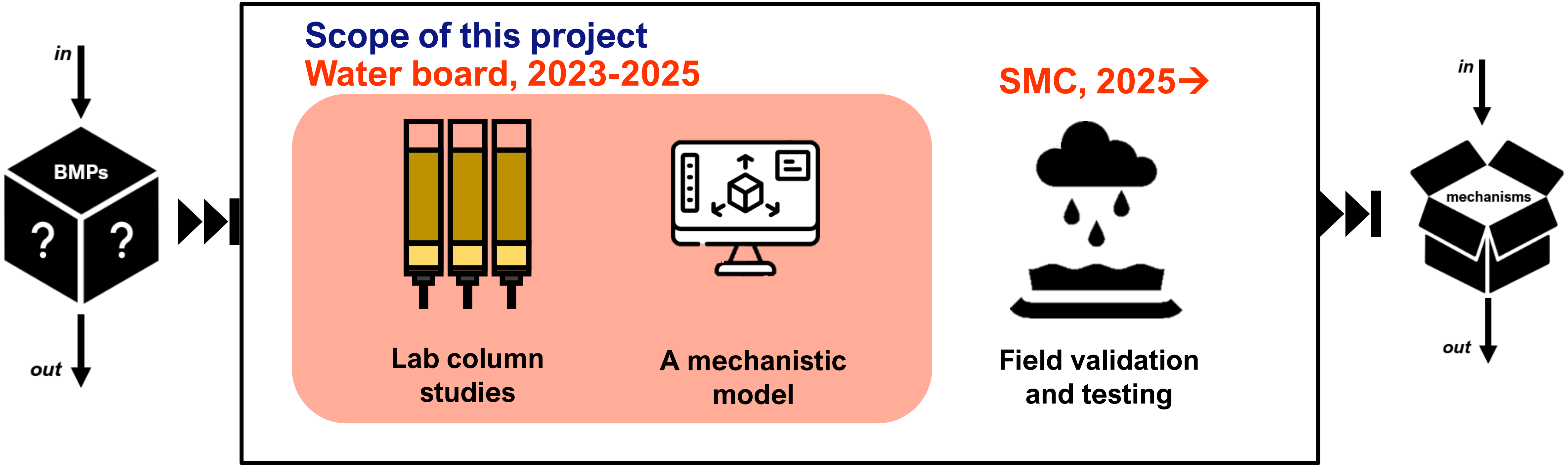
Watershed Managers

Choose the right structural BMP design that best satisfies water quality objectives

Regulators

Instill confidence in design procedures and predictions for achieving water quality goals

Approach to open the BMP “black box”



Scope of this project

Water board, 2023-2025

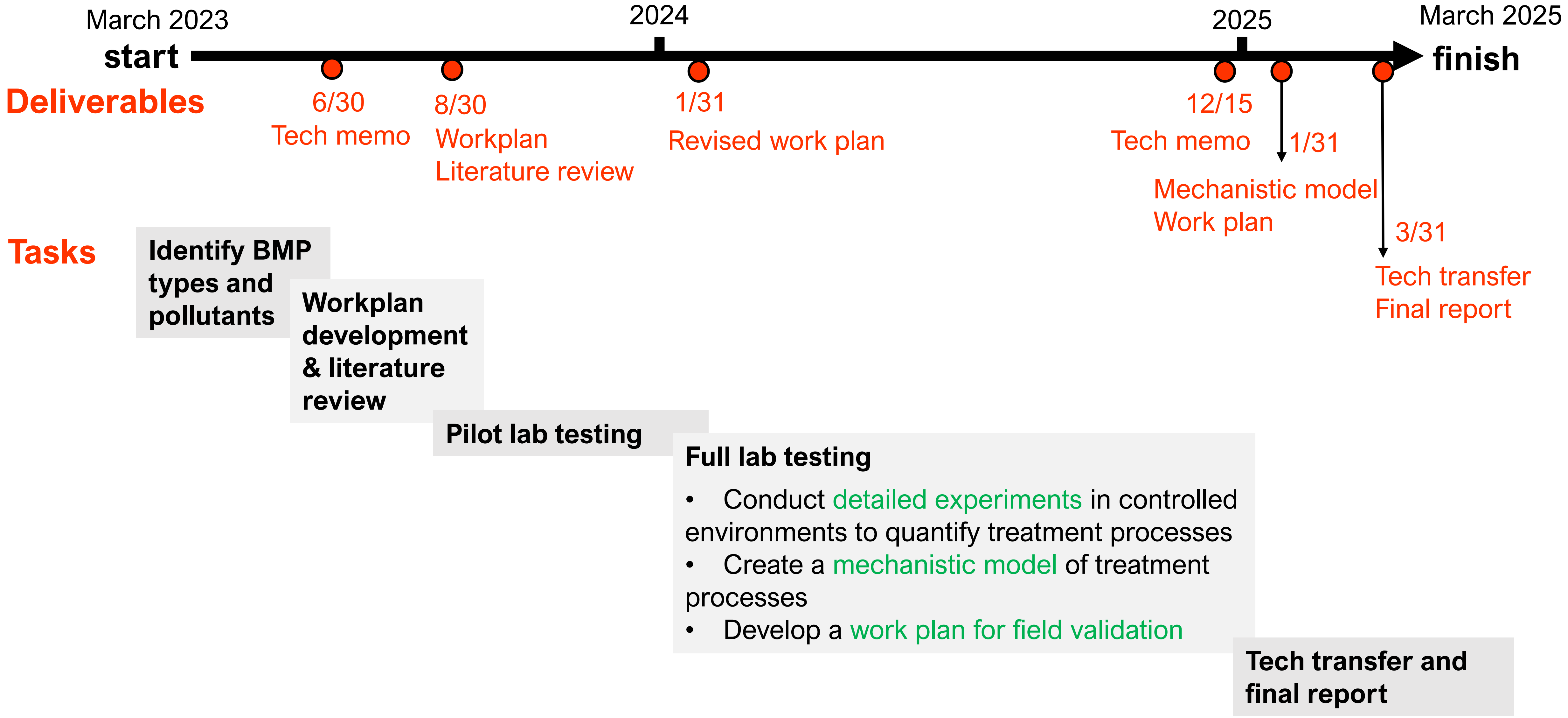
Lab column studies

A mechanistic model

SMC, 2025→

Field validation and testing

Two-year timeline



March 2023 **start**

2024

2025

March 2025 **finish**

Deliverables

6/30 Tech memo

8/30 Workplan Literature review

1/31 Revised work plan

12/15 Tech memo

1/31 Mechanistic model Work plan

3/31 Tech transfer Final report

Tasks

Identify BMP types and pollutants

Workplan development & literature review

Pilot lab testing

Full lab testing

- Conduct detailed experiments in controlled environments to quantify treatment processes
- Create a mechanistic model of treatment processes
- Develop a work plan for field validation

Tech transfer and final report

Outline

1. Overview of project goals & timeline

2. On the first deliverable: BMP and pollutants

3. Overall approach

4. Expected outcomes and potential challenges

5. Look ahead: pilot testing

We are kicking off the project!

March 2023

start

2024

2025

March 2025

finish

Deliverables

6/30

Tech memo

Task **Identify BMP types and pollutants**

BMP Recommended

- **Biofiltration**

Pollutants recommended

- **Copper (Cu^{2+}), nitrate (NO_3^-), per/poly-fluorinated substances (PFAS)**

BMP type

Biofiltration

- A common BMP to capture runoff and remove pollutants by engineered media
- **One of the few BMPs that should be able to induce all or most treatment processes**
- In-out design and use of engineered media
  - Create opportunities for quantifying pollutant treatment processes by adjusting media properties and operating conditions

Pollutants recommended

Cu^{2+}, NO_3^-, and PFAS

- **Ubiquitous** or potentially ubiquitous in the urban runoff
- **Representative**
  - Heavy metals, nutrients, and organic contaminants of emerging concern
  - Cations, anions, and neutral compounds
  - Present at very different concentration
- Expected to be treated by **different mechanisms and processes**
  - Quantify physical, chemical, and biological processes

Outline

1. Overview of project goals & timeline

2. On the first deliverable: BMP and pollutants

3. Overall approach

4. Expected outcomes and potential challenges

5. Look ahead: pilot testing

☐ Start with sorption (Cu^{2+} & PFAS)

For pilot testing, start with Cu^{2+}

- Removal mechanism is relatively **straightforward**
  - Sorption
- Easy to monitor
  - Ion selective electrode
  - Inductively coupled plasma-optical emission spectroscopy (ICP-OES)

Working tasks (Cu^{2+} as an example)

Design controlled lab column studies to quantify Cu^{2+} sorption/desorption in synthetic stormwater.

Column Configuration

Media Selection

Column Operation

Data Collection

- Transparent
- Cylindrical
- Dimensions
    - Diameter: 4"
    - Length: 36”


Column 5
Column 1
Column 2
Column 3
Column 4
Column 6
PA Sand R1
PA Sand R2


FULL CYLINDERS
CILINDROS LLENOS
EMPTY CYLINDERS
1320
1660
8566

Working tasks

Design controlled lab column studies to quantify Cu^{2+} sorption/desorption in synthetic stormwater.

Column Configuration

- Transparent
- Cylindrical
- Dimensions
    - Diameter: 4"
    - Length: 24”

Media Selection

Identify **properties of media** that affect Cu^{2+} removal

We are not trying to come up with optimal media!

Column Operation

Assess how **operating conditions** affect Cu^{2+} removal

Data Collection

- Monitor
- Measure

Parameter identification for column study design

Cu^{2+}

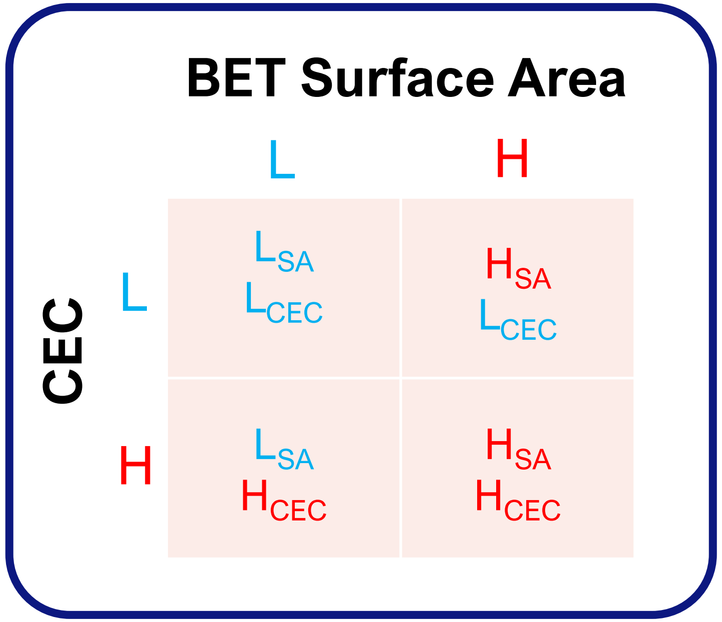
Sorption

Media Properties	R	P	D
Sorption		✗	
Anion exchange capacity	✗		
Cation exchange capacity (CEC)	✓		
Bulk porosity	✗		
BET surface area	✓		
Internal porosity			✗
Compaction			✗
Particle size			✗
Redox property	✗		
Hydrophobicity	✗		
Leachable organic carbon	✗		
pH_{zpc}		✗	✗
BOD	✗		
Microbes: nitrifier, methanogens	✗		

Operating Conditions	R	P	D
Flow (Q):compaction & ponding depth	✓		
Infiltration rate (*i*)		✗	
Rainfall time			✗
Rainfall frequency	✓		
Antecedent drying days			✗
Residence time		✗	✗
Internal water storage	✗		
Aerobic/anaerobic conditions	✗	✗	
Pollutant concentration	✓		

Selection criteria: relevance (R), practicability/transferability (P), and duplicity (D)

Media properties



BET Surface Area

CEC

	L	H
L	L_{SA} L_{CEC}	H_{SA} L_{CEC}
H	L_{SA} H_{CEC}	H_{SA} H_{CEC}

BET surface area

- Specific surface area, including the area of internal pores
- Range from <10 to near 1000 m^2/g

Cation exchange capacity (CEC)

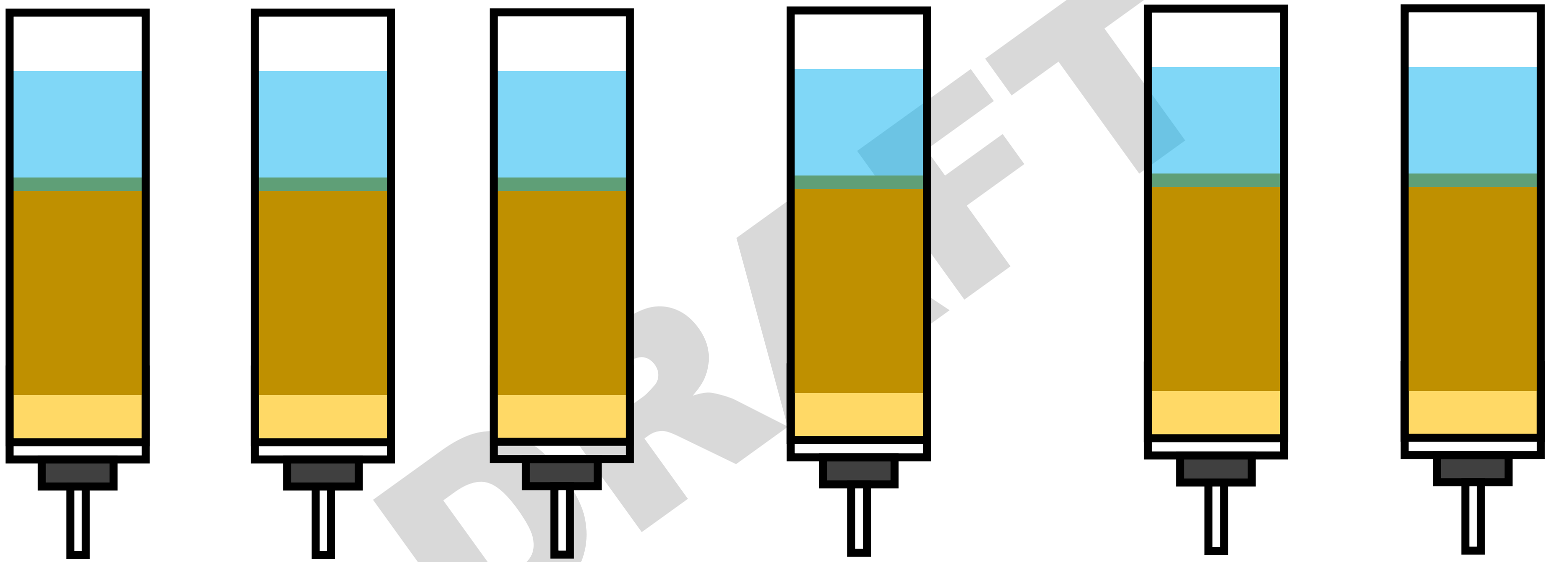
- The capacity of media to retain cations on its surface
- <0.05 to 0.5 mmol/g

Columns

6 columns, duplicate, 12 in total

Training

Validation



L_{CEC} L_{SA} — Sand only

H_{CEC} L_{SA} — Sand X% resin

L_{CEC} H_{SA} — Sand X% biochar1

H_{CEC} H_{SA} — Sand X% biochar2 ↕ or Sand X% resin X% biochar1

H_{CEC} H_{SA} — Sand nX% biochar2

H_{CEC} H_{SA} — Sand X% sbiochar2

Operating conditions

				$[Cu^{2+}]$	
Rainfall frequency (ν)				L	H
	L	**Flow rate (Q)**	L	L_{C0} L_Q L_ν	H_{C0} L_Q L_ν
			H	L_{C0} H_Q L_ν	H_{C0} H_Q L_ν
	H	**Flow rate (Q)**	L	L_{C0} L_Q H_ν	H_{C0} L_Q H_ν
			H	L_{C0} H_Q H_ν	H_{C0} H_Q H_ν

Outline

1. Overview of project goals & timeline

2. On the first deliverable: BMP and pollutants

3. Overall approach

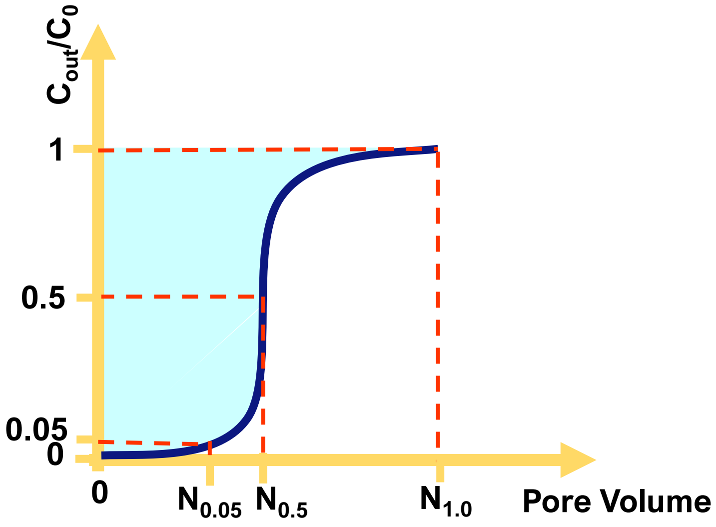
4. Expected outcomes and potential challenges

5. Look ahead: pilot testing

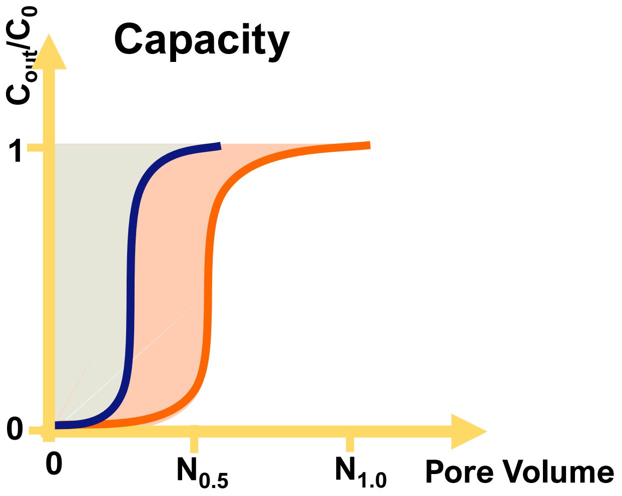
Expected outputs

What information will we get?

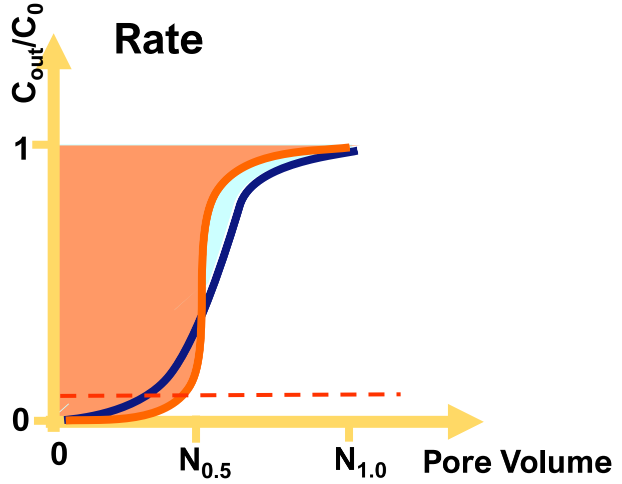
Breakthrough curves



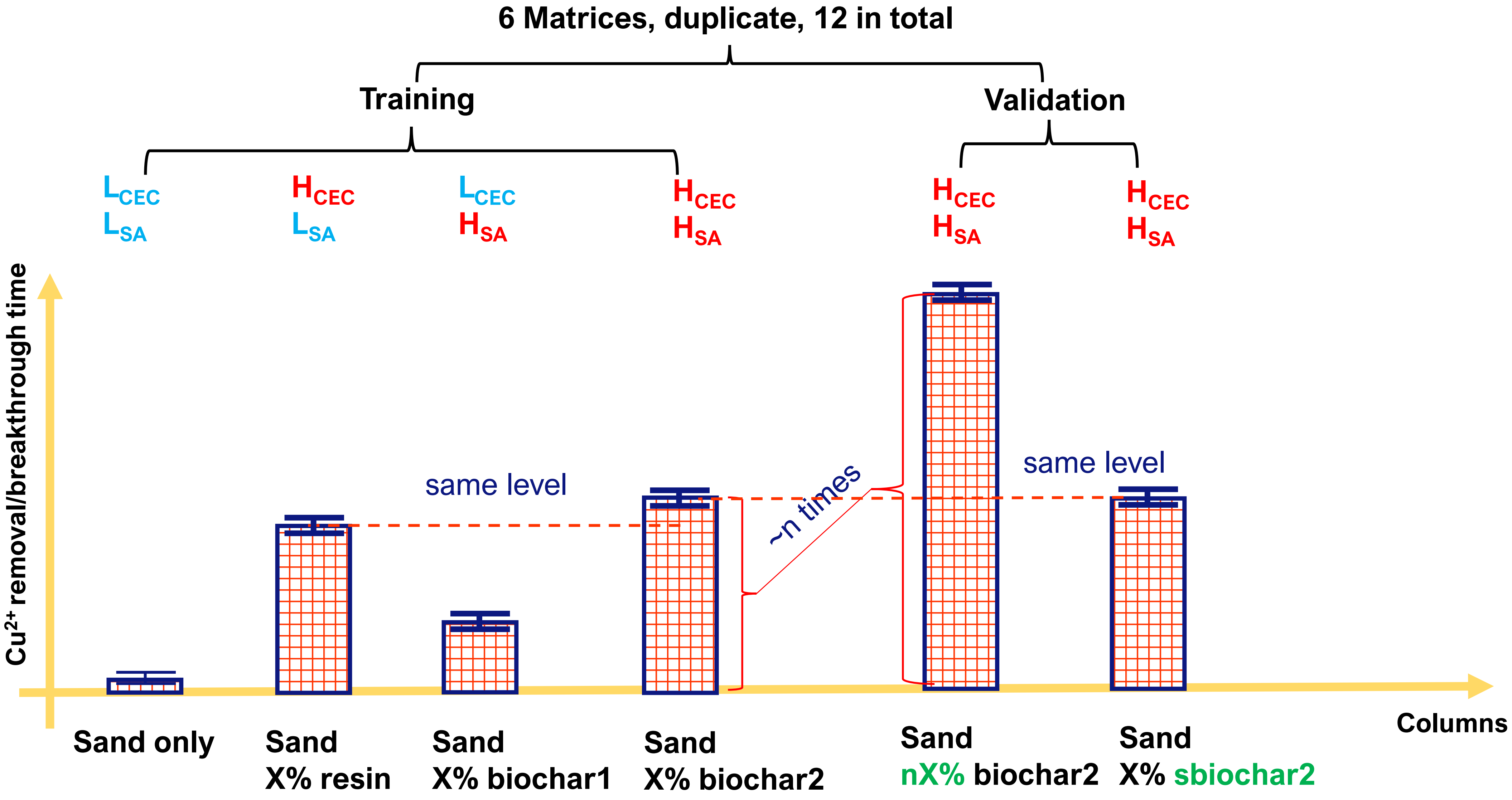
Capacity



Rate



Expected outputs



Potential Challenges

- **Uncertainties regarding the time for the breakthrough curve**
- **To balance between the quantity of sample/data for modeling and analysis cost.**
- Suggestions?

Outline

1. Overview of project goals & timeline

2. On the first deliverable: BMP and pollutants

3. Overall approach

4. Expected outcomes and potential challenges

5. Look ahead: pilot testing

Look ahead schedules

March 2023 **start** — 2024 — 2025 — March 2025 **finish**

Deliverables

- 6/30 Tech memo
- 8/31 Workplan, Literature review
- 1/31 Revised workplan

Tasks

Identify BMP types and pollutants ✓

The BMP and pollutants recommended

- **Biofiltration**
- **Pollutants: copper (Cu^{2+}), nitrate (NO_3^-), per/poly-fluorinated substances (PFAS)**

Work plan& literature review ↻

- Literature review is underway
- Investigate **hydrological conditions** and **properties of media**

Pilot lab testing 🕒

- Experimental design for **pilot study** is underway for quantifying treatment processes through **controlled lab column studies**

Goals of pilot testing (until January 31st, 2024)

- **Setup and test columns**
  - Figure out all logistics and procedures of running column tests
    - Column packing
    - Sampling frequency and volume, etc.
- **Getting initial sets of data**
  - **Is the data set what we anticipated?**
  - **Could the data serve the model?**
    - Fine-tune the experimental/sampling plan
- **Refine the scope for full testing**

Review on decisions

☐ Pollutants recommended

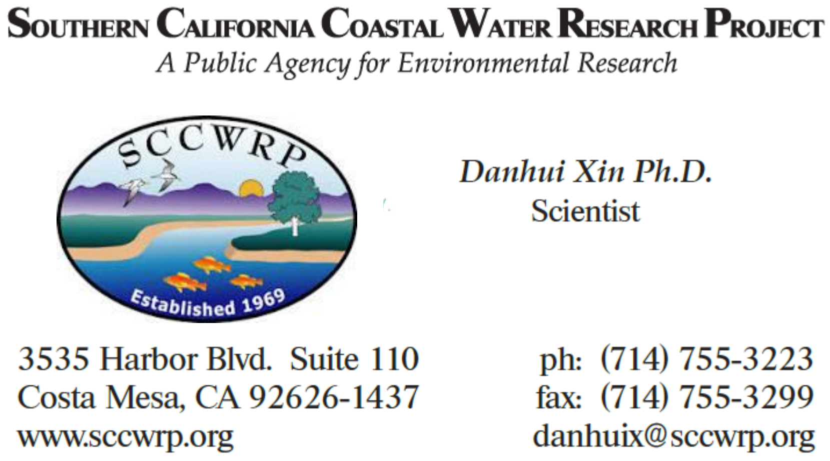
Cu^{2+}, NO_3^-, and PFAS

- (Potentially) **ubiquitous** in the urban runoff
- **Representative:** metal, nutrient, contaminants of emerging concerns
- Expected to be treated by **different mechanisms and processes**

☐ Start with Cu^{2+} for pilot tests

- Removal mechanism is straightforward → sorption

Thank you for listening!



SOUTHERN CALIFORNIA COASTAL WATER RESEARCH PROJECT
A Public Agency for Environmental Research

SCCWRP
Established 1969

Danhui Xin Ph.D.
Scientist

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APPENDIX E. SMC PRESENTATIONS

Appendix E

Southern California
STORMWATER MONITORING
Coalition

CALIFORNIA
Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

Project Overview

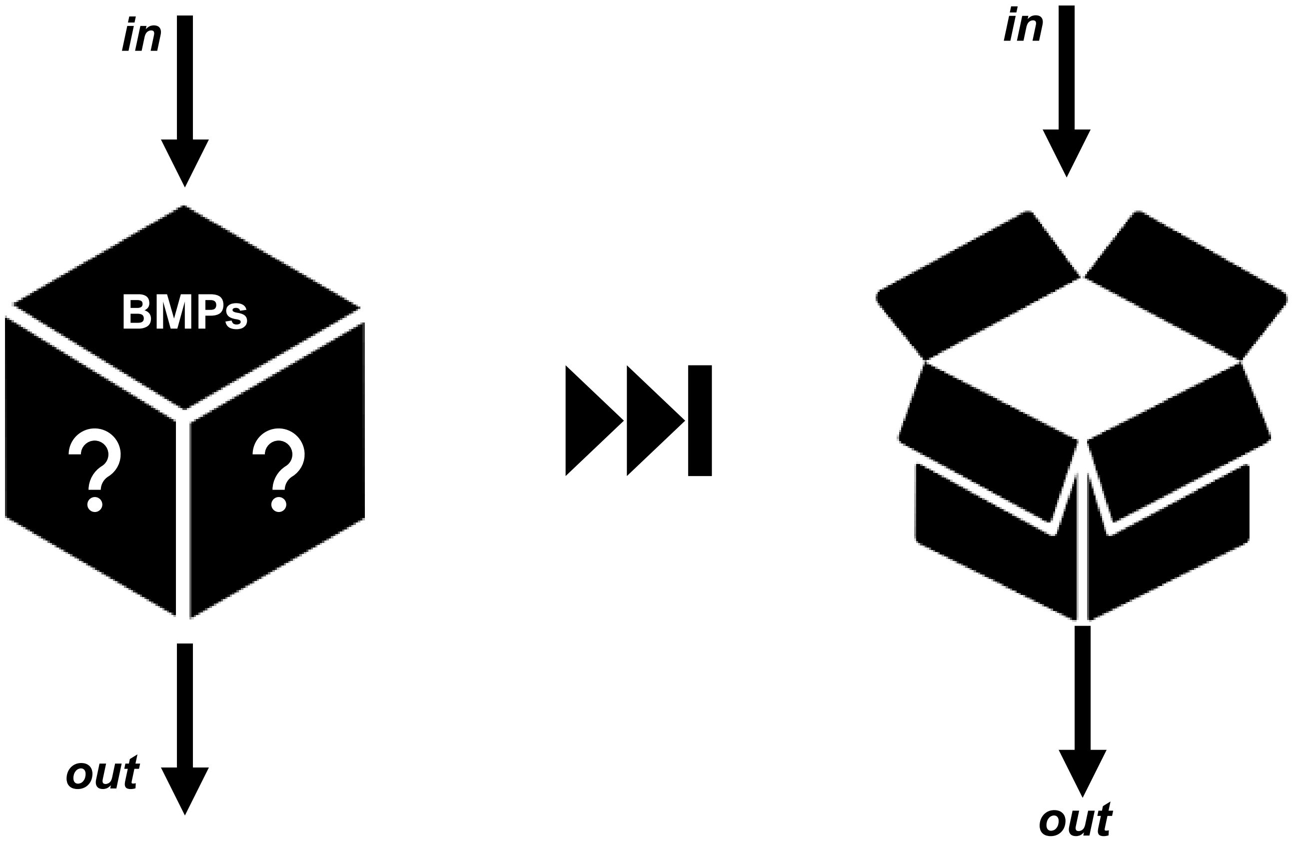
Mechanistic Studies on Pollutant Removal by Stormwater BMPs

SCCWRP
Established 1969

Danhui Xin, Ph.D.
SCCWRP Scientist
June 2023

Informational Update

Goal: Open the “black box”



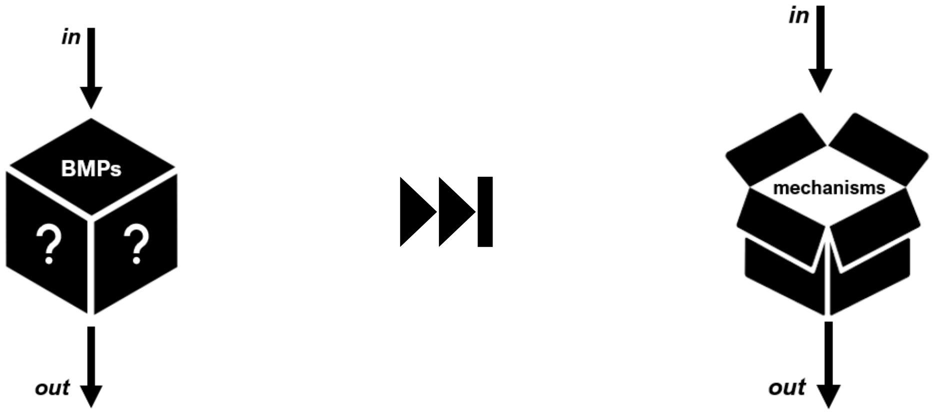
Mechanisms
Processes

- Sedimentation
- Sorption
- Ion exchange
- Oxidation/reduction
- Biodegradation

…

We aim to identify and **quantify** the treatment **mechanisms and processes** for removing different **pollutants** from stormwater within a structural BMP.

Why care?



- Experience-based design
- Unpredictable performance

- **Process-based design**
- **Predictable performance**

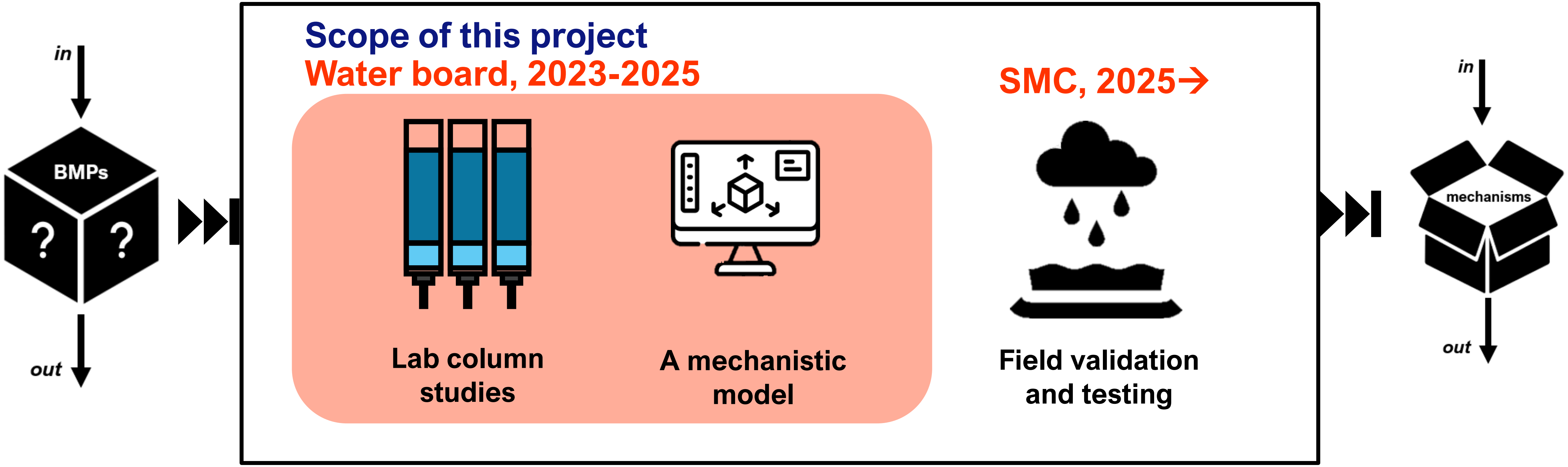
BMP Engineers

Design treatment procedures that match pollutant removal goals

Watershed Managers

Choose the right structural BMP design that best satisfies water quality objectives

Approaches and scope



Scope of this project

Water board, 2023-2025

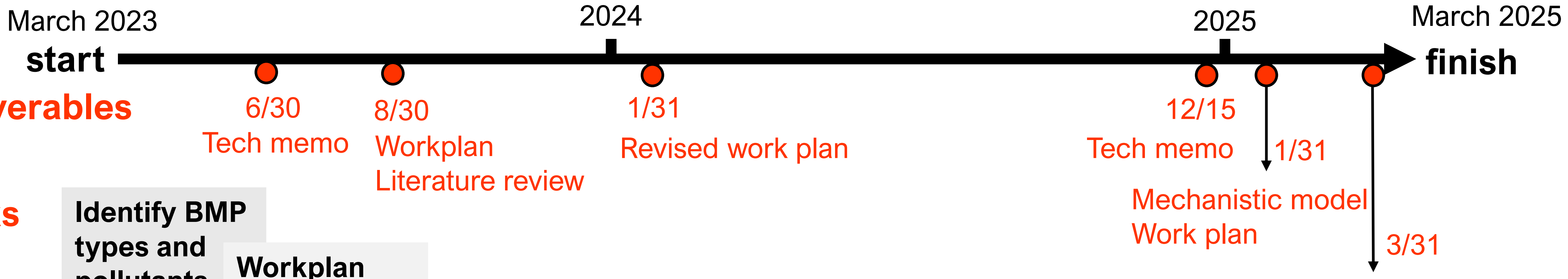
SMC, 2025→

Lab column studies

A mechanistic model

Field validation and testing

Two-year timeline



March 2023
start

2024

2025

March 2025
finish

Deliverables

6/30
Tech memo

8/30
Workplan
Literature review

1/31
Revised work plan

12/15
Tech memo

1/31
Mechanistic model
Work plan

3/31
Tech transfer
Final report

Tasks

Identify BMP types and pollutants

Workplan development & literature review

Preliminary lab testing
Pilot experiments to quantify treatment processes

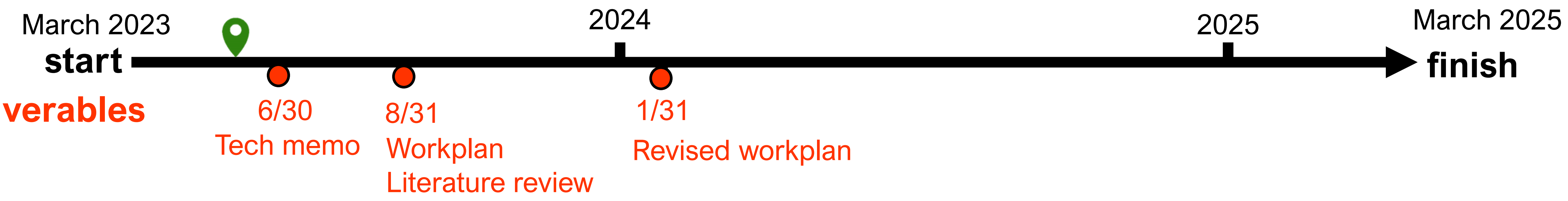
Full lab testing

- Conduct detailed experiments in controlled environments to quantify treatment processes
- Create a mechanistic model of treatment processes
- Develop a work plan for field validation

Tech transfer and final report

SOUTHERN CALIFORNIA
STORMWATER MONITORING
COALITION

Where we are



March 2023 **start**

2024

2025

March 2025 **finish**

Deliverables

6/30
Tech memo

8/31
Workplan
Literature review

1/31
Revised workplan

Tasks

Identify BMP types and pollutants ✓

Biofiltration

Pollutants: Start with copper (Cu^{2+})

- Representative of heavy metals, commonly detected in urban runoff

Work plan& literature review

- Literature review is underway
- Investigate operating conditions and **properties of media (not media types)**

Preliminary lab testing

- Experimental design is underway for quantifying treatment processes through controlled lab column studies

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Scientist, Chemistry
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Stay tuned and thank you!

Informational Update

Mechanistic Studies on Pollutant Removal by Stormwater BMPs

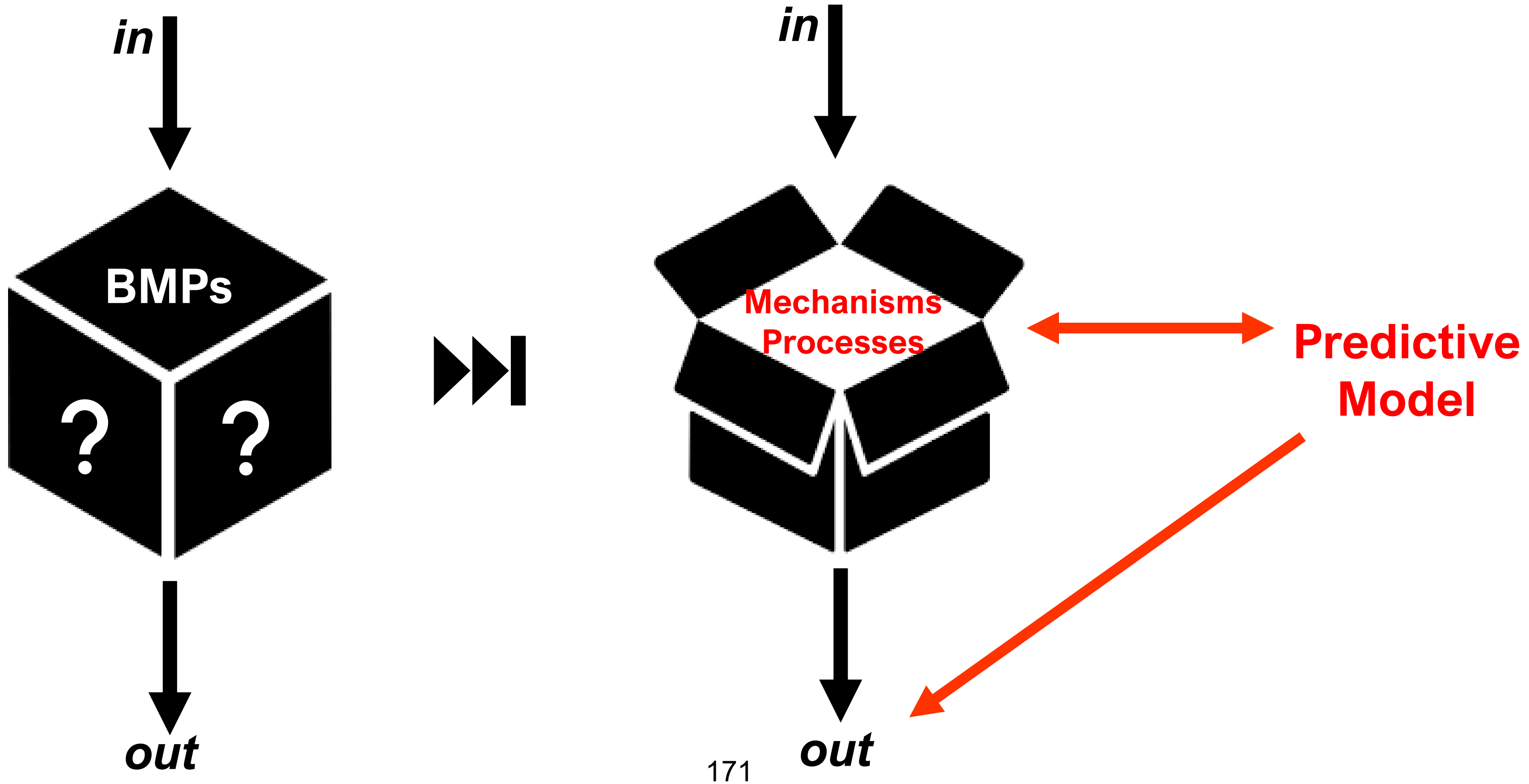
Danhui Xin, Ph.D.

SCCWRP Scientist

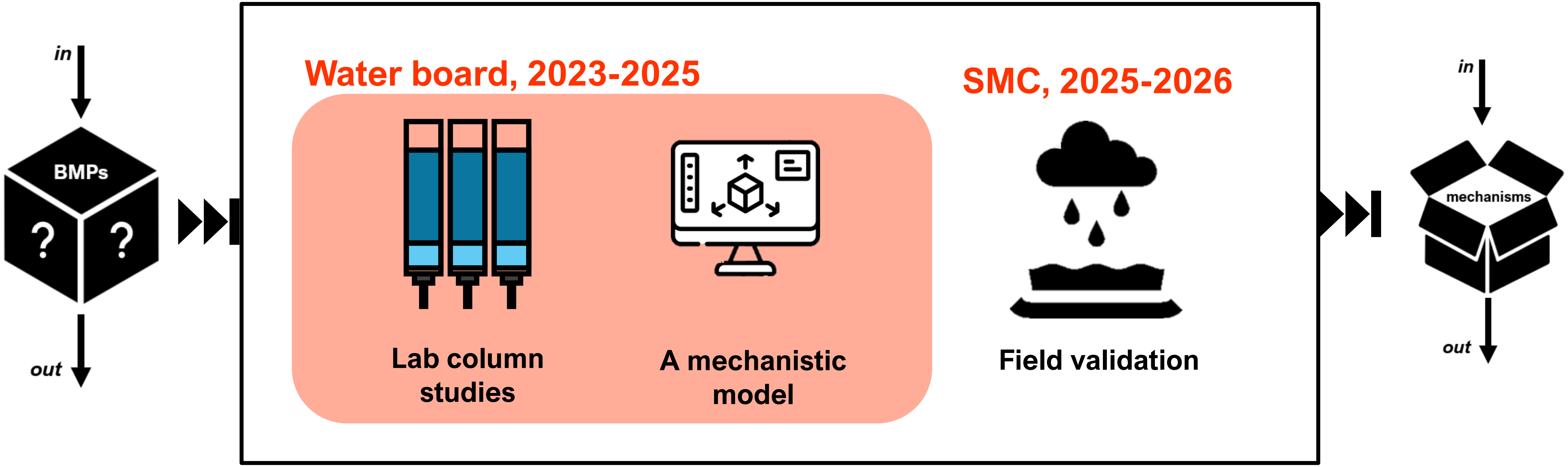
September 2023

Goal

We aim to identify and quantify the treatment **mechanisms and processes** for removing different **pollutants** from stormwater within a structural BMP and build **tools** to predict performance .



Approaches and scope



Water board, 2023-2025

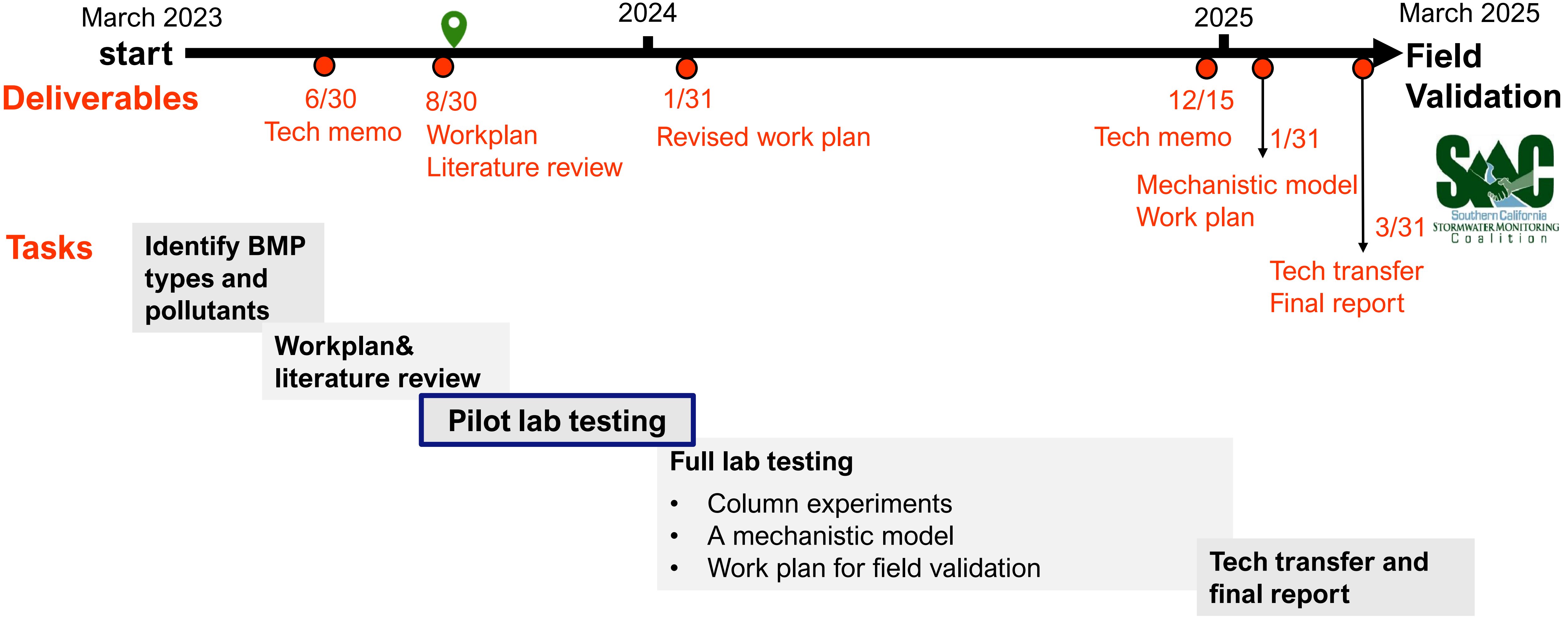
Lab column studies

A mechanistic model

SMC, 2025-2026

Field validation

Timeline



March 2023

start

2024

2025

March 2025

Field Validation

Deliverables

6/30
Tech memo

8/30
Workplan
Literature review

1/31
Revised work plan

12/15
Tech memo

1/31
Mechanistic model
Work plan

3/31
Tech transfer
Final report

Southern California
STORMWATER MONITORING
Coalition

Tasks

Identify BMP types and pollutants

Workplan& literature review

Pilot lab testing

Full lab testing

- Column experiments
- A mechanistic model
- Work plan for field validation

Tech transfer and final report

2019 SMC Research Agenda Expert Panel

Karen Ashby
Larry Walker & Assoc.
Monitoring Specialist

Drew Kleis
City of San Diego
Regulated Community

Allen Davis
Univ. of Maryland
Civil/Enviro. Engineer

Jody Harwood
Univ. of South Florida
Microbiology/ Public Health

David Senn
SFEI
Water Quality Chemist

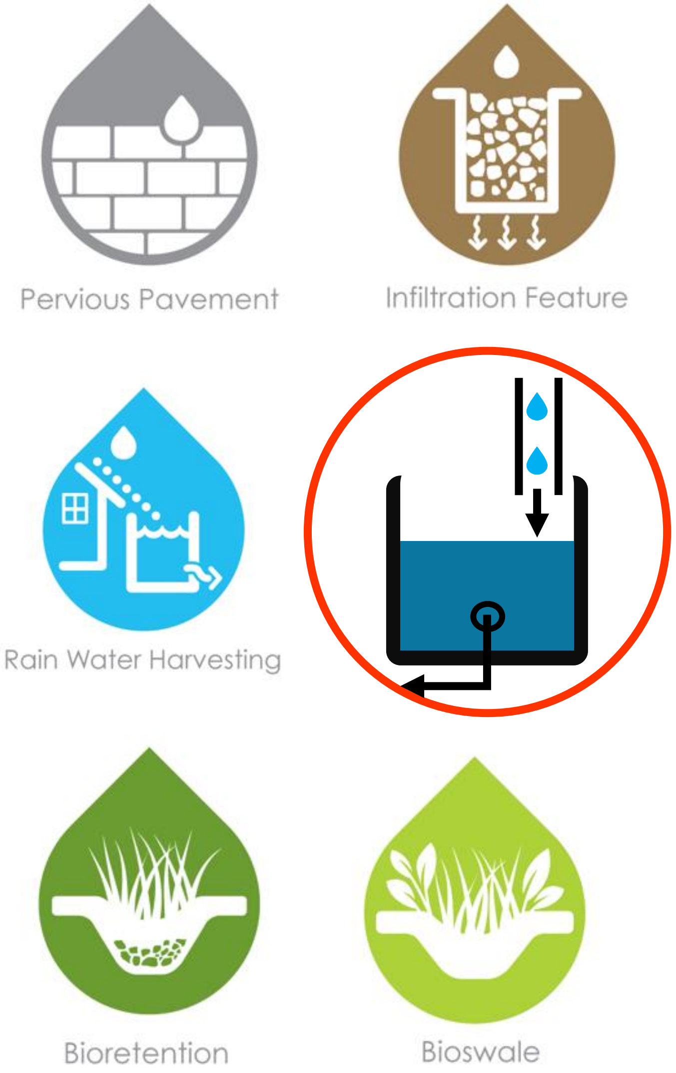
Greg Gearheart
State WRCB
Information Specialist

Shelley Luce
Heal the Bay
Environmental Advocacy

Teri Hogue
Colorado School of Mines
Modeling

Pete Ode
CA Dept. of Fish & Wildlife
Ecology/Biology

BMP type



Biofiltration

- A common BMP
- **One of the few BMPs that should be able to induce all or most treatment processes**
- Use of engineered media and flow-through design
  - Create opportunities for quantifying pollutant treatment processes by **adjusting media properties and operating conditions**

Pollutants

Copper (Cu), nitrate (NO_3^-), and per/poly-fluorinated substances (PFAS)

- **Ubiquitous** or potentially ubiquitous in the urban runoff
- **Representative**
  - Heavy metals, nutrients, and organic compounds of emerging concern
  - Cations, anions, and neutral compounds
- Expected to be treated by **different mechanisms and processes**

Knowledge gaps

Where we are

Cu → Sorption	PFAS → Sorption	NO_3^- → Biodegradation
Relatively good removal through sorption	Limited PFAS monitoring data for stormwater	Highly variable but consensus on the importance of anaerobic zone

Knowledge gaps

Connection between measurable medium properties and treatment processes connection	Very limited prior studies in the context of stormwater BMP	Quantitative evaluation of the abundance/activity of denitrifiers

Next steps

- **Pilot test work plan submitted to State Board 8/30/2023**
- **Pilot column testing will focus on sorption process**

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Danhui Xin, Ph.D.
Scientist, Chemistry
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Stay tuned and thank you!

CALIFORNIA
Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

Southern California
STORMWATER MONITORING
Coalition

Informational Update

Mechanistic Studies on Pollutant Removal by Stormwater BMPs

SCCWRP
Established 1969

Danhui Xin, Ph.D.

SCCWRP Scientist

December 2023

Scope

Phase I: Lab-based (2023-2025)

CALIFORNIA
Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

Column studies

A mechanistic model

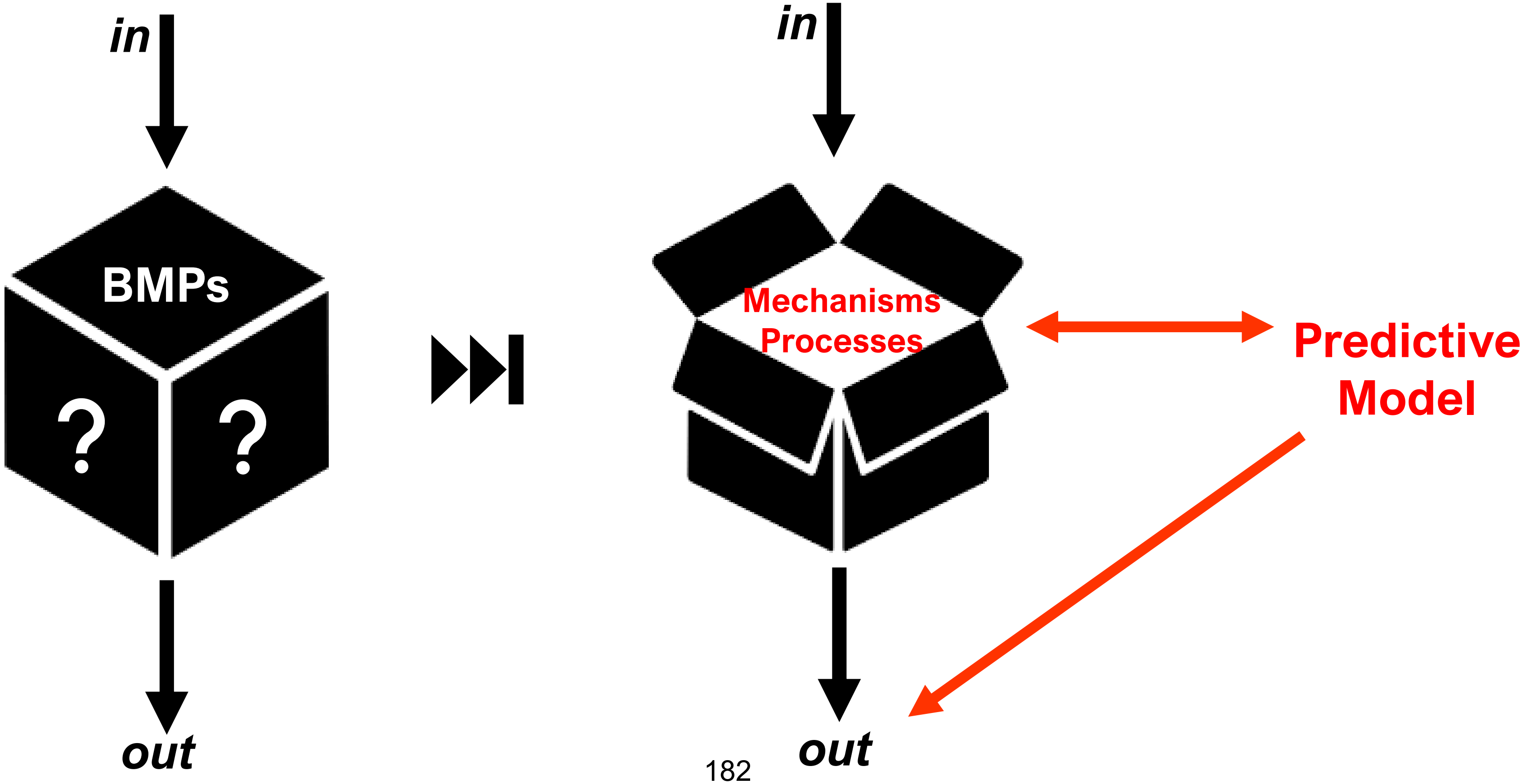
Phase II: Field-based (2025-2026)

SMC
Southern California
STORMWATER MONITORING
Coalition

Field validation

Goal

We aim to identify and quantify the treatment **mechanisms and processes** for removing different **pollutants** from stormwater within a structural BMP and build tools to predict performance .

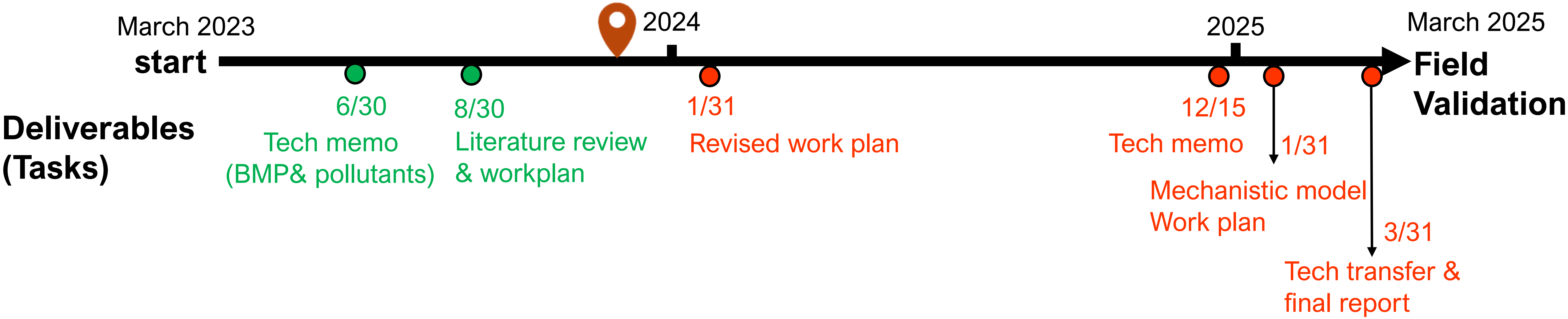


Approach

A BMP of interest

Unpack its pollutant removal mechanisms & processes through lab column studies

Timeline of lab studies (Water Board)



March 2023
start

2024

2025

March 2025
Field Validation

Deliverables (Tasks)

6/30
Tech memo
(BMP& pollutants)

8/30
Literature review
& workplan

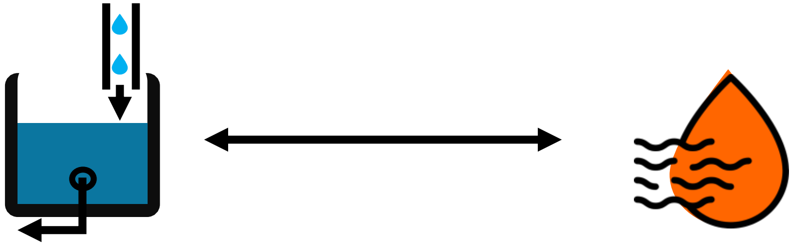
1/31
Revised work plan

12/15
Tech memo

1/31
Mechanistic model
Work plan

3/31
Tech transfer &
final report

☑ Task 1: Identify BMP types and pollutants



Biofiltration

Pollutants

- Dissolved copper (Cu)
- Nitrate (NO_3^-)
- Per/poly-fluorinated substances (PFAS)

☑ Task 2: Literature review

Cu → Sorption

Gap: The connection between measurable medium properties and treatment processes

PFAS → Sorption

Gap: Very limited prior studies in the context of stormwater BMP

Pilot testing is focused on the sorption process.

↓

Hypotheses

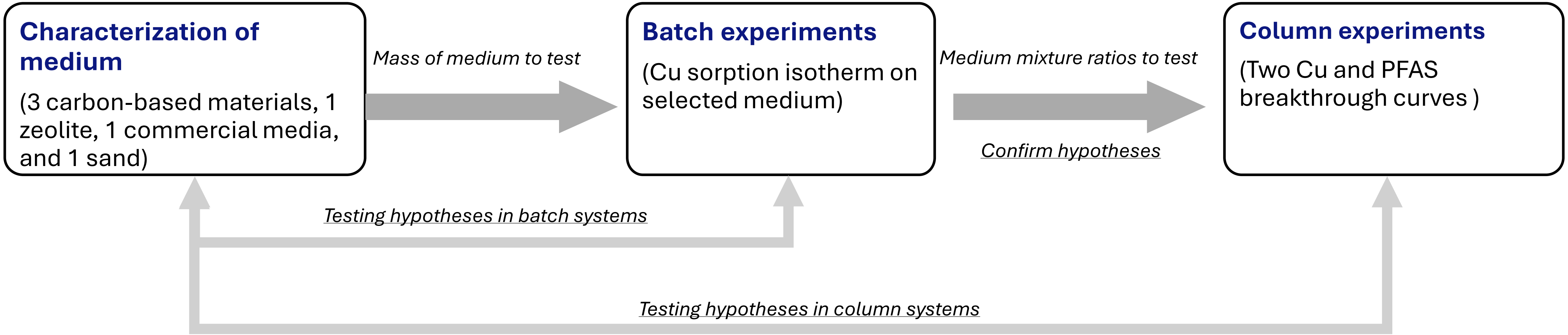
☑ Task 2: Hypotheses

Connecting measurable medium properties and pollutant treatment performance of BMP

Hypothesis	Practical Interpretation
The **cation exchange capacity (CEC)** and/or **specific surface area** of the medium determine the **capacity** of cationic (e.g., Cu^{2+}) and organic pollutant (e.g., PFAS) sorption.	*Do measurements of engineered media (**CEC** and/or **specific surface area)** give meaningful, quantifiable indications of **the capacity** to remove Cu or PFAS?*
The **zeta potential** and/or **hydrophobicity** of the medium influence the **affinity** of cationic (e.g., Cu^{2+}) and organic pollutant (e.g., PFAS) sorption.	*Do measurements of engineered media (**zeta potential** and/or **hydrophobicity**) give meaningful, quantifiable indications of **the extent to which** Cu or PFAS will be removed by sorption?*

Task 2: Workplan for pilot testing

Goal: Narrow down the scope of column testing



Characterization of medium

(3 carbon-based materials, 1 zeolite, 1 commercial media, and 1 sand)

Mass of medium to test

Batch experiments

(Cu sorption isotherm on selected medium)

Medium mixture ratios to test

Confirm hypotheses

Column experiments

(Two Cu and PFAS breakthrough curves)

Testing hypotheses in batch systems

Testing hypotheses in column systems

Task 3: Active pilot testing in progress

Runoff collection

Media characterization

Batch experiments

Column construction

Next quarter

- **Updates on the results from pilot testing**
  - Media characterization
  - Batch and initial column experiments

Elizabeth Fassman-Beck, Ph.D.
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Danhui Xin, Ph.D.
Scientist, Chemistry
danhuix@sccwrp.org

Stay tuned and thank you!

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Water Boards
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REGIONAL WATER QUALITY CONTROL BOARDS

Southern California
STORMWATER MONITORING
Coalition

Informational Update

Mechanistic Studies on Pollutant Removal by Stormwater BMPs

SCCWRP
Established 1969

Danhui Xin, Ph.D.
SCCWRP Scientist
June 2024

Outline

❑ **Project Overview**

❑ **Key Outcomes**

- Methods for CEC measurement should be prescribed in the design guidance
- Media CEC is a promising predictor of Cu sorption
- Breakthrough curves indicate the lifetime of media for Cu sorption

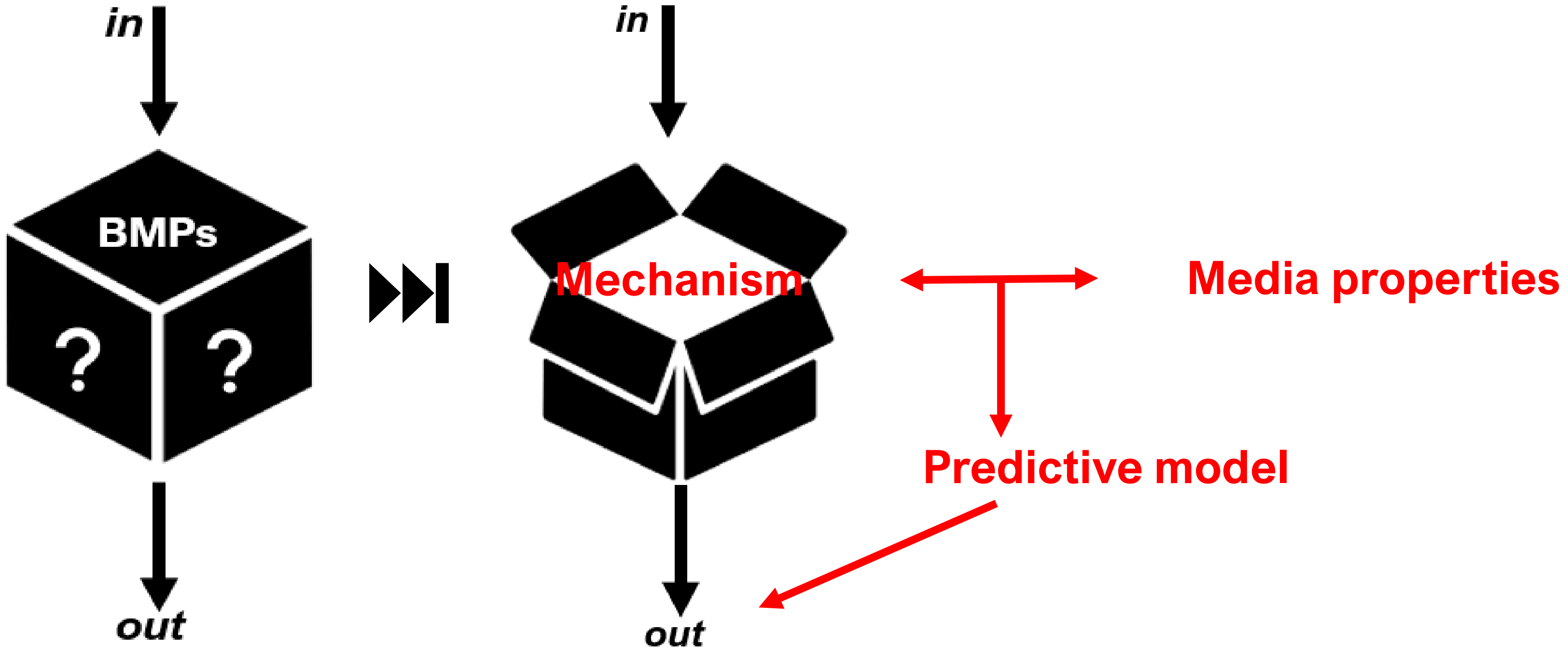
❑ **Current Activities & Next Steps**

- Doubled column capacity and started sample for PFOA and PFOS

Goal

We aim to identify and quantify the treatment **mechanisms** for removing different **contaminants** from stormwater within a structural BMP and build **tools** to predict performance.

→ Sorption of dissolved copper and PFAS (PFOA and PFOS) in biofiltration media
→ Mechanistic model that predicts contaminant removal during storm events



Scope: Sorption of Cu and PFAS in biofiltration media

Phase I: Lab-based (2023-2025)

CALIFORNIA
Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

Lab experiments

Mechanistic model

Phase II: Field-based (July 2024-2026)

SMC
Southern California
STORMWATER MONITORING
Coalition

Field validation

Phase 1: Lab-based

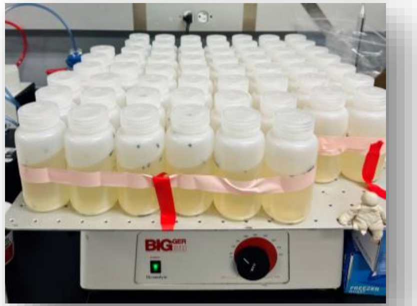
☑ **Media characterization**

☑ **Batch experiments**

Column experiments
- ☑ **Pilot-scale**
- ⟳ **Full-scale**

Model development

Quantify properties of candidate media components



Select media and determine ratios of materials to mix in columns

Work through logistics and prove the experimental approach

Outline

☐ Project Overview

☐ Key Outcomes

- Methods for CEC measurement should be prescribed in the design guidance
- Media CEC is a promising predictor of Cu sorption
- Breakthrough curves indicate the lifetime of media for Cu sorption

☐ Current Activities & Next Steps

- Doubled column capacity and started sample for PFOA and PFOS

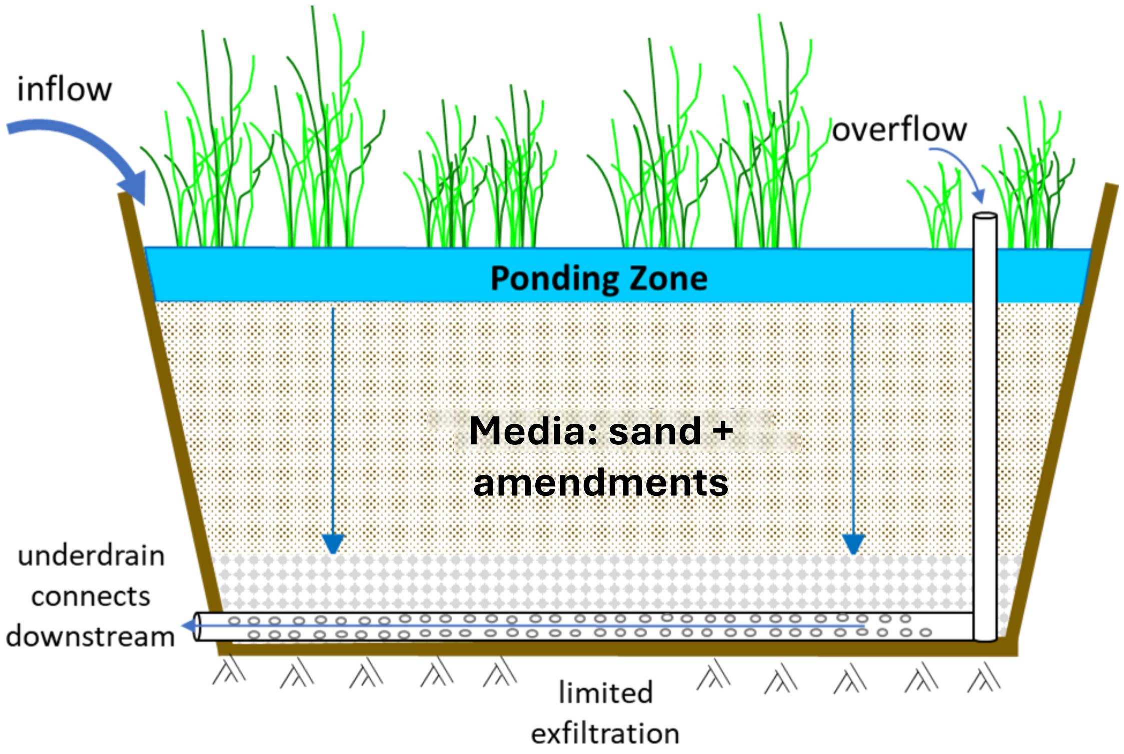
Literature review outcome: properties-sorption

Media Property	What does it measure?
Cation exchange capacity (CEC)	a measure of the amount of positively charged species that might stick to a surface *How many parking spots are there?*
BET surface area	a measure of the internal surface area of a material *How big is the parking lot?*

↓

Hypothesis	Practical Interpretation
The CEC and/or BET surface area of the medium determines the capacity of cationic (e.g., Cu^{2+}) and organic pollutant (e.g., PFAS) sorption.	*Do measurements of media (CEC and/or BET surface area) give meaningful, quantifiable indications of Cu or PFAS removal in biofiltration?*

Media components tested



Biofiltration BMP

Sand:
Pacific Aggregates (PA) concrete sand
<u>ASTM C-33</u>

Candidate amendments:

biochars

regenerated activated carbon (RAC)

zeolite

Media characterization

design guidance

mechanism: sorption

Media type	Media name	pH	Loss of Ignition	Olsen-P	NO_3^--N	CEC_{Ba}*	CEC_X	BET SA**
			weight%	mg-P/kg	mg-N/kg	meq/100g	meq/100 g	m^2/g
Sand	PA	7.94±0.00	0.13	<1	1.52	<2	2.08	–
Mineral	Zeolite	9.61±0.03	3.8	<20	20.0	7.6	28.3	15.16
Char	Rogue	9.58±0.04	74.6	1324	0.8	15.0	25.3	546.51
	Hydrophobic	7.75±0.07	66.4	292	2.2	13.7	7.7	237.05
	Hydrophilic	5.99±0.10	53.4	1232	20	21.0	19.8	443.62
	RAC	9.10±0.57	1.4	424	2.2	3.6	5.5	840.50

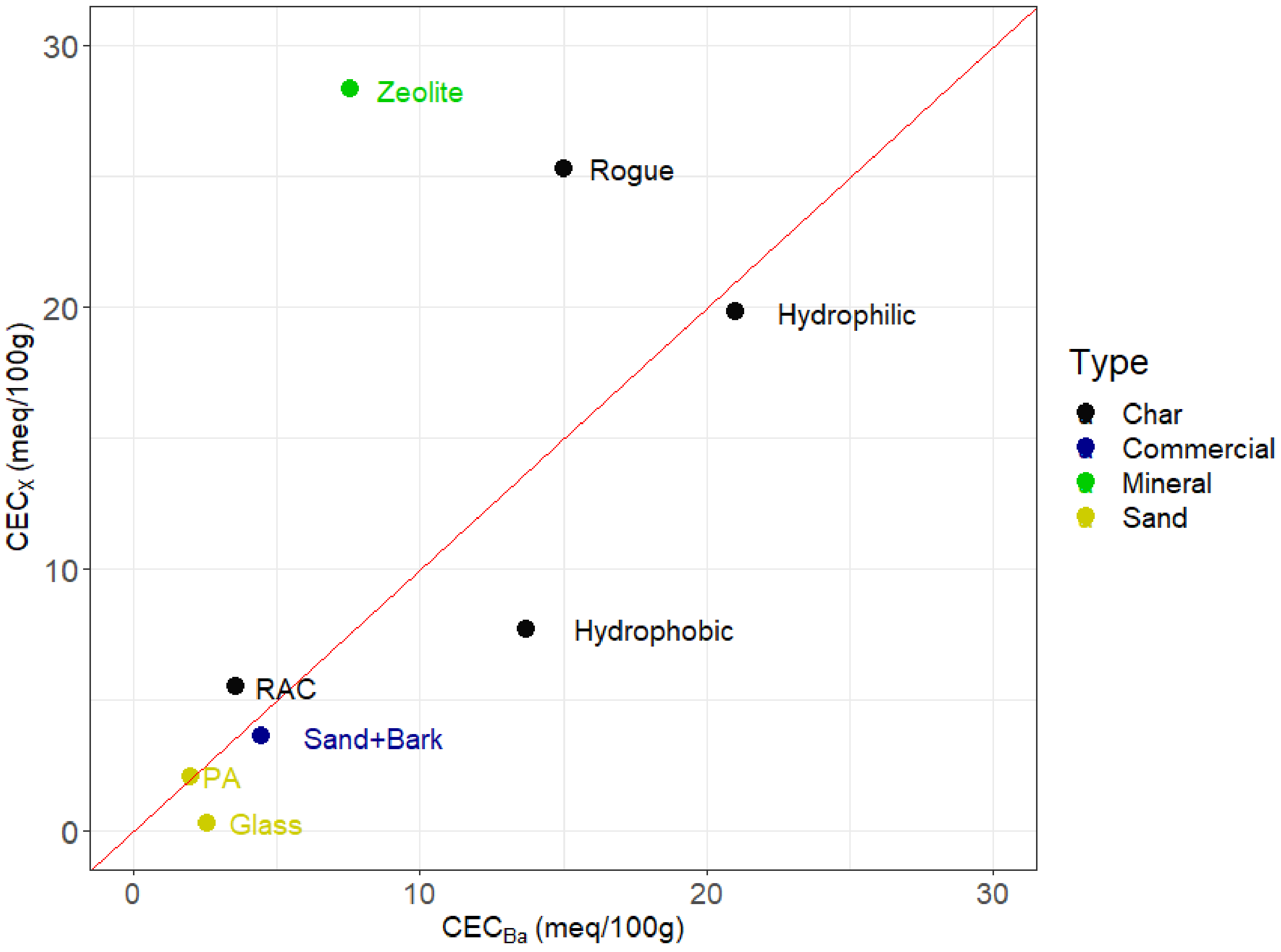
*CEC: Cation exchange capacity; **BET SA: A specific surface area

❑ **Covered a broad range of properties**

- properties — treatment mechanism – treatment effectiveness

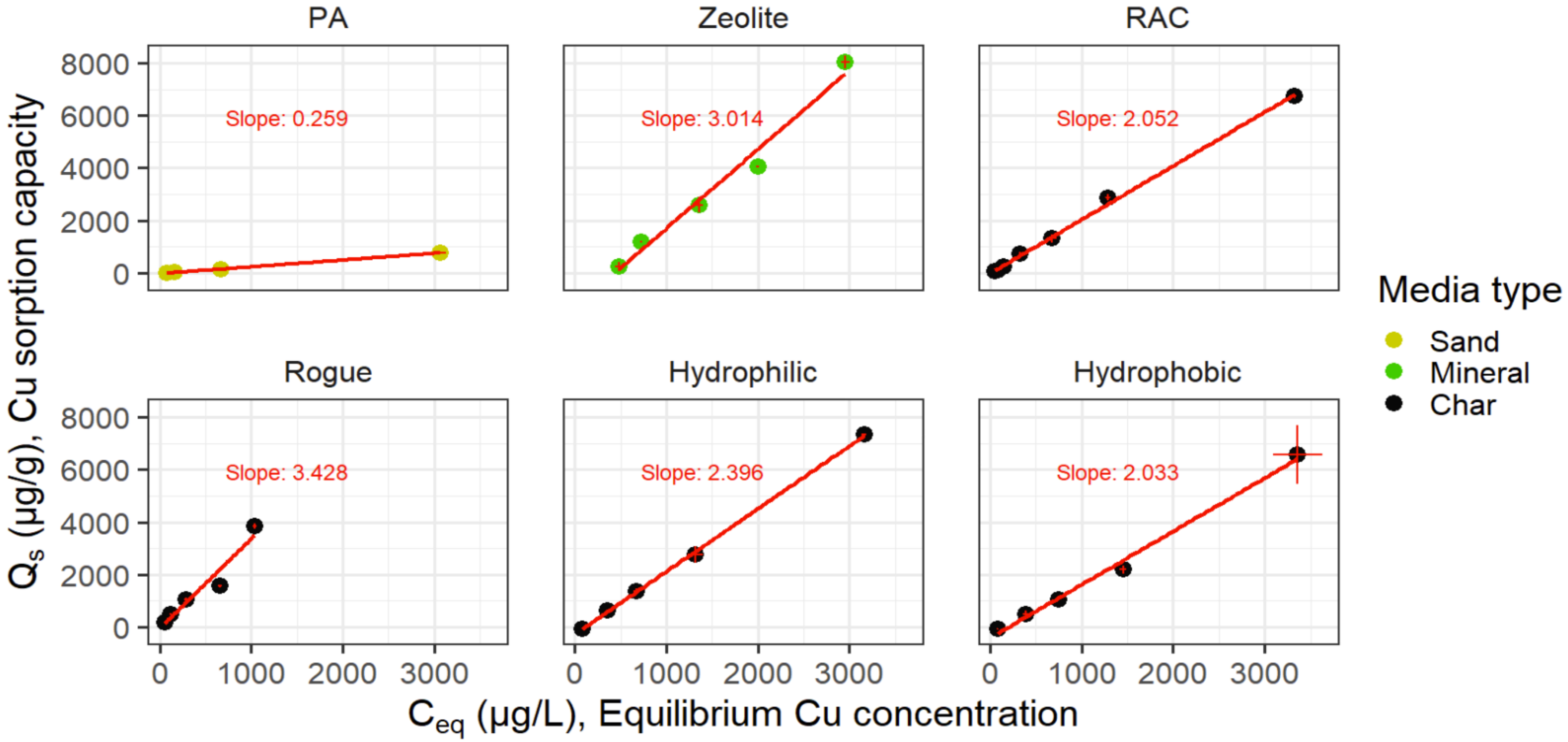
CEC methods

- >5 different methods
- Design guidance doesn't specify the method
- We compared two common methods
  - CEC_{Ba} : Barium saturation followed by calcium replacement, quantified based on calcium loss
  - CEC_X : Ammonium saturation, quantified based on the sum of replaced K, Ca, Mg, Na



❑ **Methods for CEC should be prescribed in the design guidance**

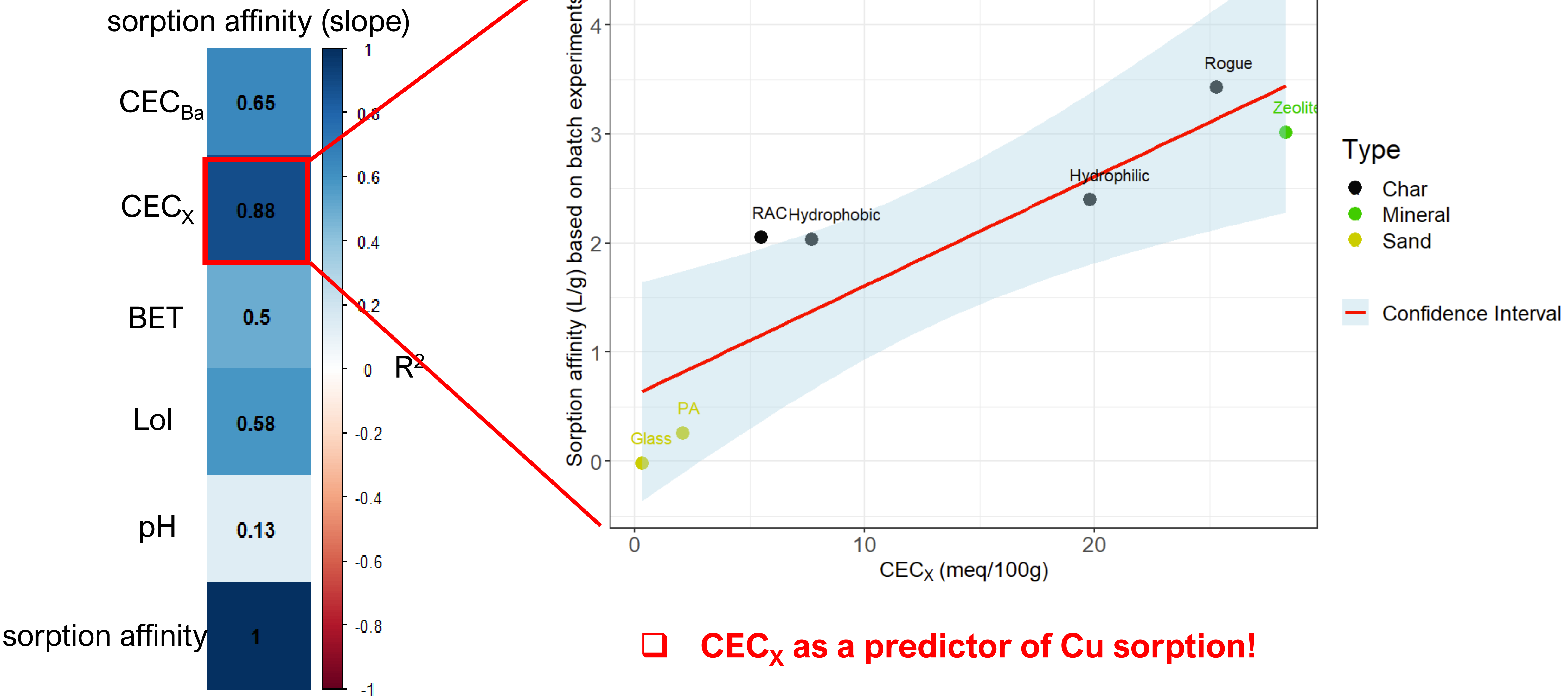
Cu sorption to media in batch reactors



- ❑ **Linear isotherms (R^2>0.90) can predict the sorption capacity of a material under specific Cu concentrations**
- ❑ **Isotherms inform ratios of materials to mix in columns**
- ❑ **Slopes represent the affinity of Cu to each material**

Media properties vs. Cu sorption

Correlation analysis



❑ **CEC_X as a predictor of Cu sorption!**

Outline

❑ **Project Overview**

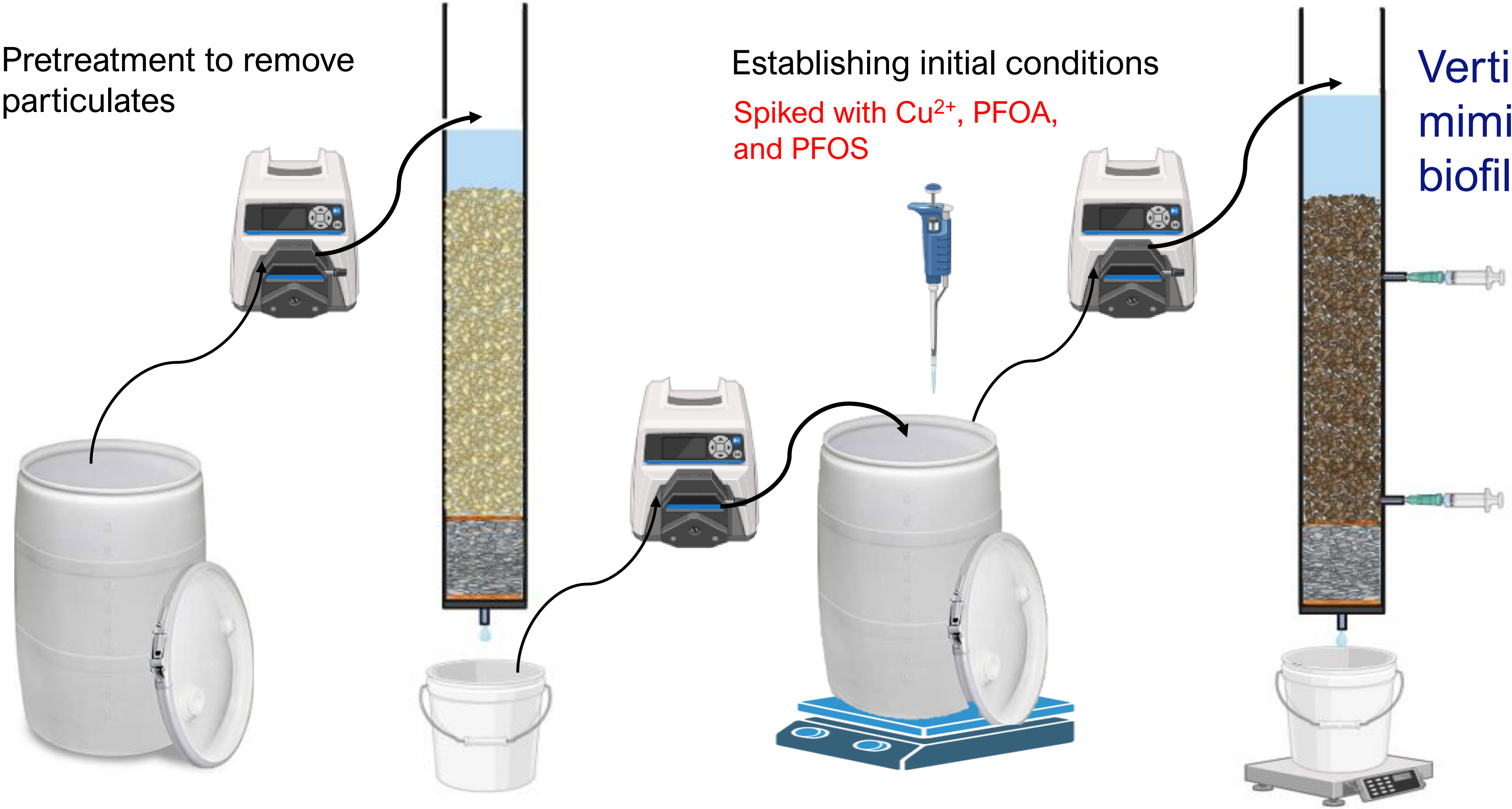
❑ **Key Outcomes**

- Methods for CEC measurement should be prescribed in the design guidance
- Media CEC is a promising predictor of Cu sorption
- Breakthrough curves indicate the lifetime of media for Cu sorption

❑ **Current Activities & Next Steps**

- Doubled column capacity and started sample for PFOA and PFOS

Spiked runoff for columns



Pretreatment to remove particulates

Establishing initial conditions

Spiked with Cu^{2+}, PFOA, and PFOS

Vertical profiles mimicking biofiltration

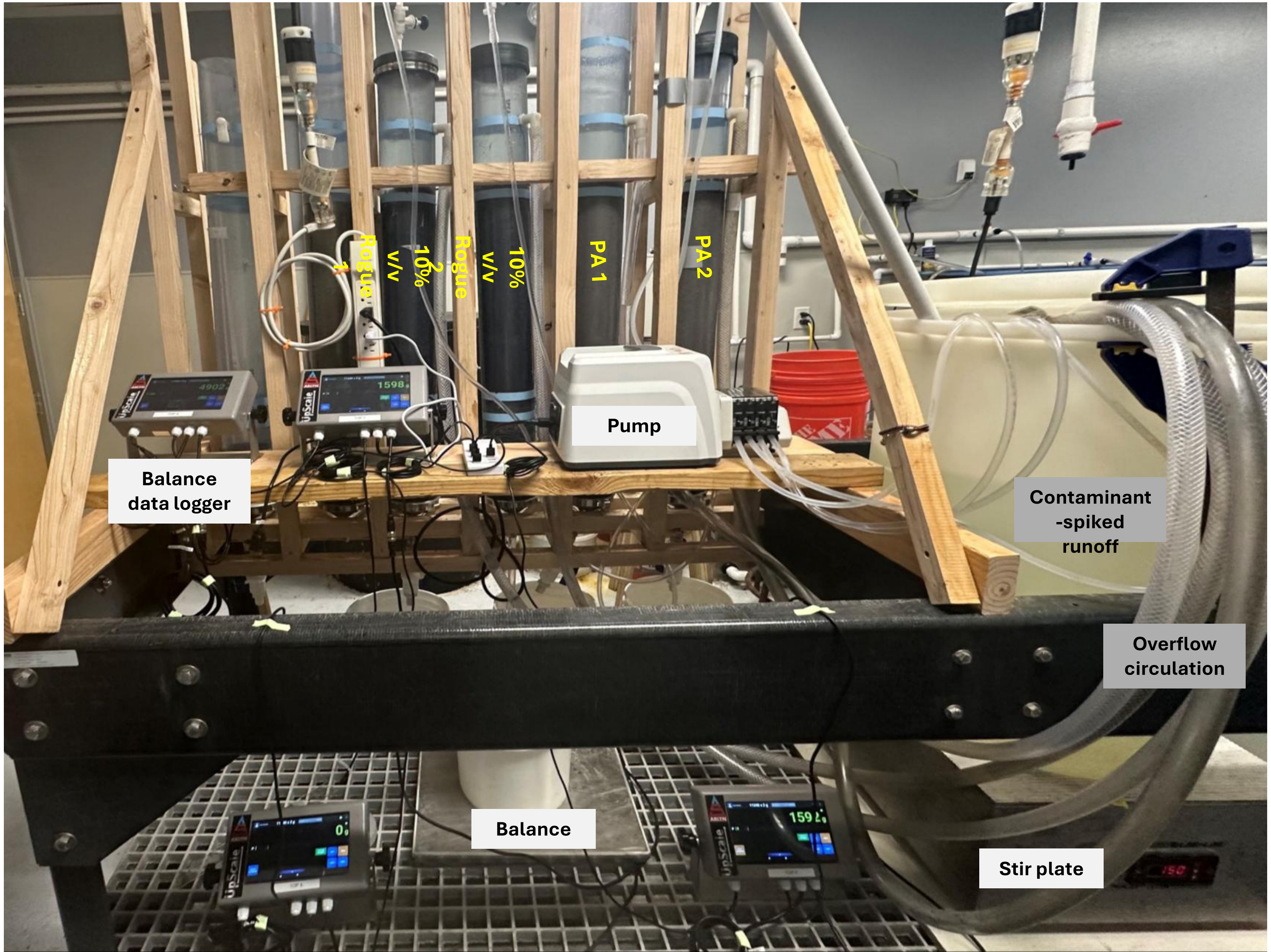
ASR collected from parking lot

Glass-sand filter

Contaminant-spiked runoff

Column experiment

Column setup



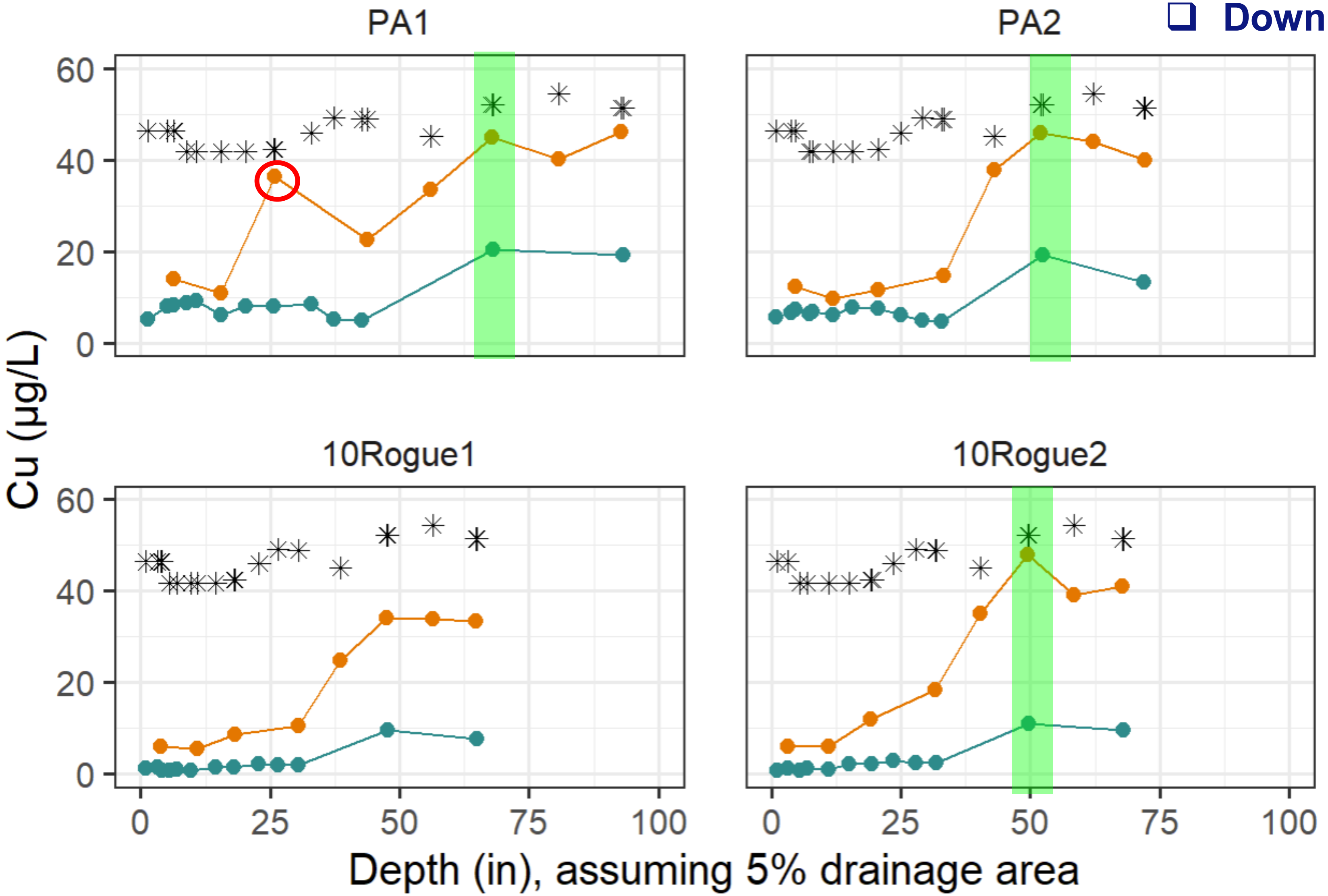
- 4 columns: 2 compositions in duplicates
- Sampled for Cu only in the pilot phase
- Flow rate was monitored (30-60 in/h)

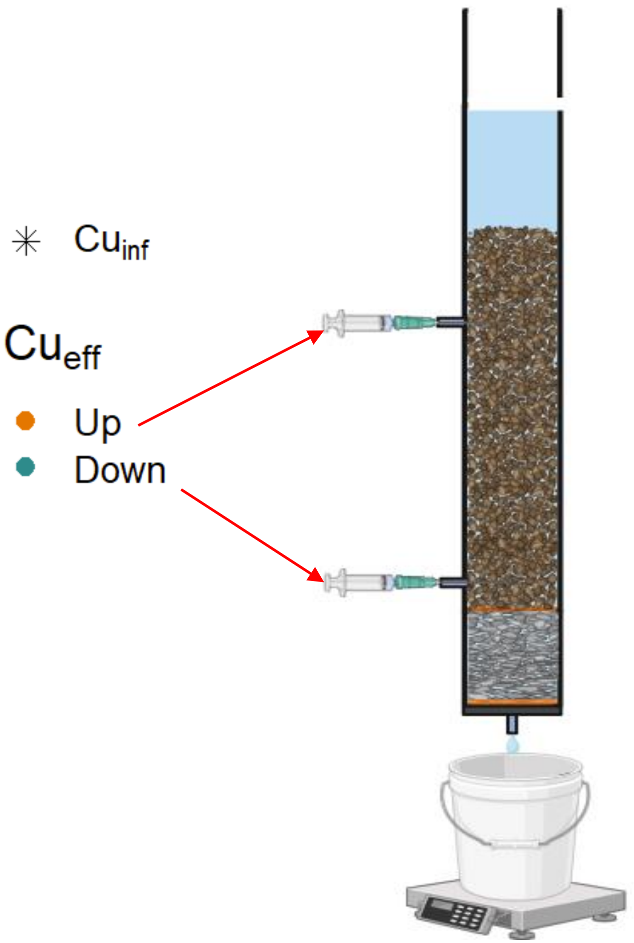
Cu breakthrough curves

☐ **Up ports reached breakthroughs**
- “Breakthrough”: when effluent = influent conc.

☐ **Breakthroughs indicate the lifetime of media for Cu sorption**
- 50-70 in (5-7 years, assuming 10 in/yr)

☐ **Down ports started to breakthrough**





Outline

❑ Project Overview

❑ Key Outcomes

- Methods for CEC measurement should be prescribed in the design guidance
- Media CEC is a promising predictor of Cu sorption
- Breakthrough curves indicate the lifetime of media for Cu sorption

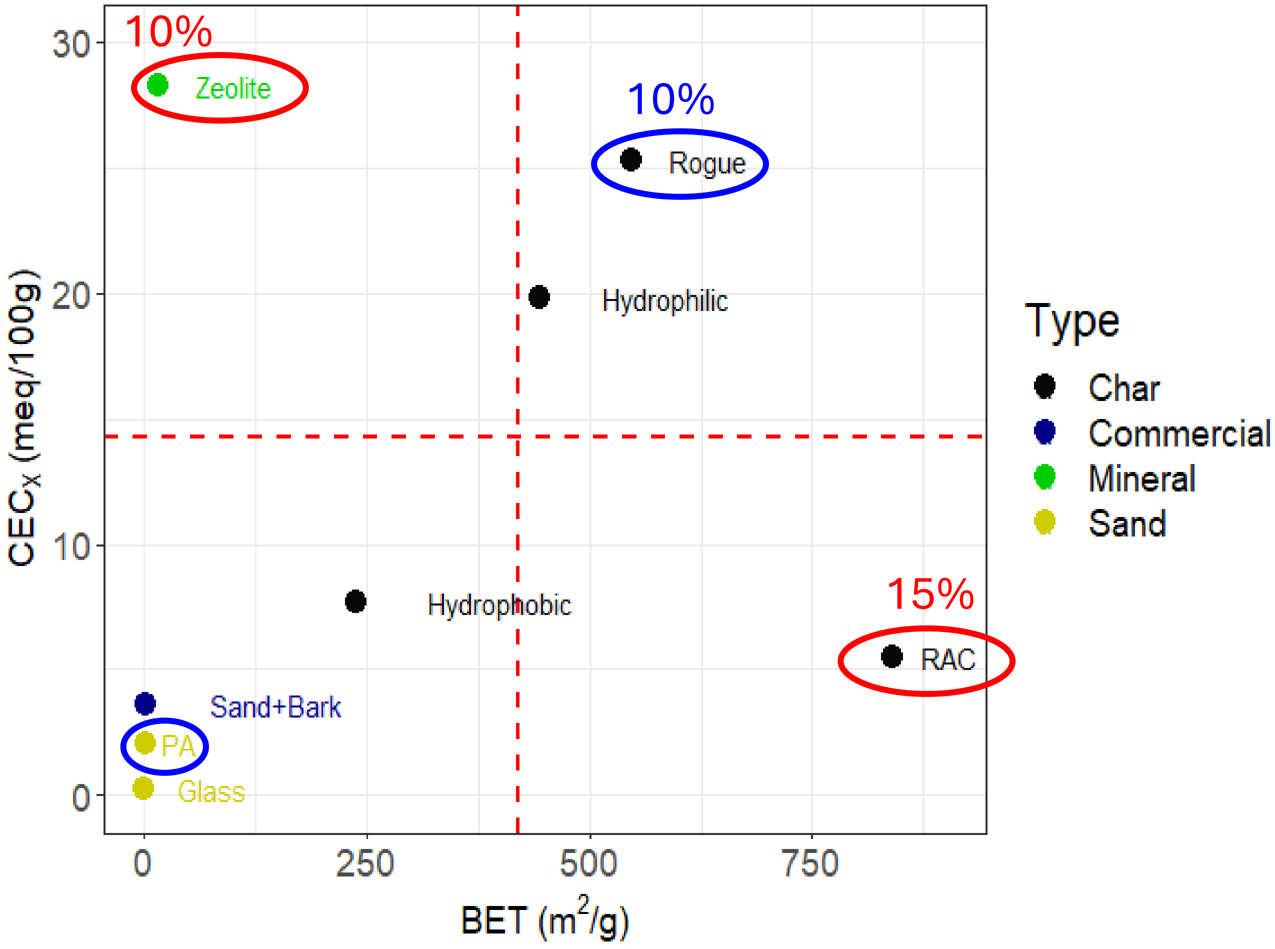
❑ Current Activities & Next Steps

- Doubled column capacity and started sample for PFOA and PFOS

Current activities

❑ Doubled column capacity

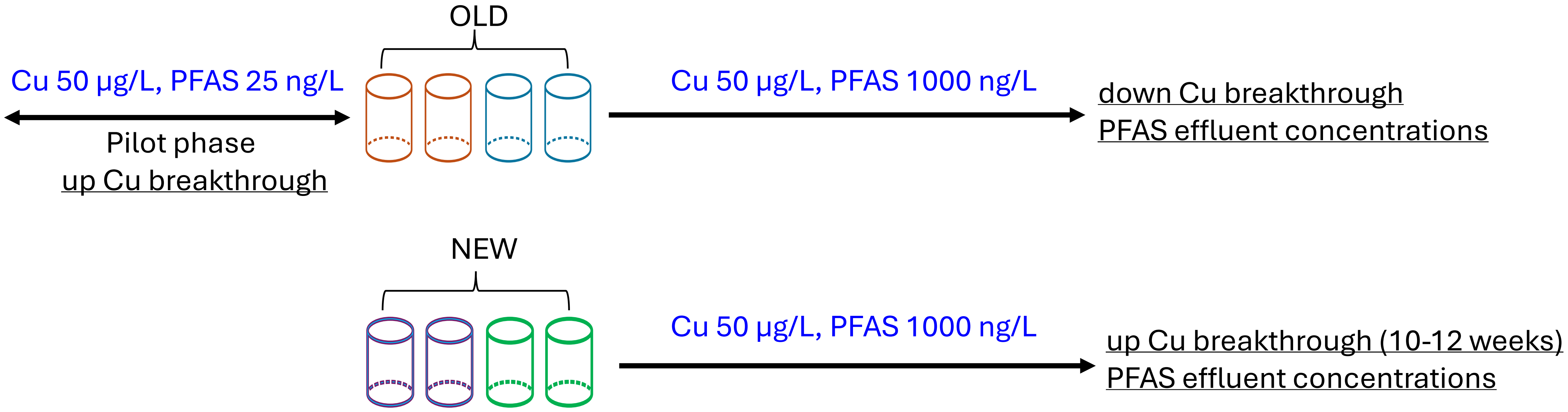
- 8 columns: 4 media compositions in duplicate



Current activities

❑ Augmented PFOA and PFOS

- Continue Cu (~50 µg/L)
- PFOA and PFOS (1000 ng/L)
    - Started sample for PFAS



OLD

Cu 50 µg/L, PFAS 25 ng/L

Pilot phase

up Cu breakthrough

Cu 50 µg/L, PFAS 1000 ng/L

down Cu breakthrough

PFAS effluent concentrations

NEW

Cu 50 µg/L, PFAS 1000 ng/L

up Cu breakthrough (10-12 weeks)

PFAS effluent concentrations

Next steps

- ❑ **Field study initiation from July**
  - SCCWRP will reach out to member agencies individually for monitoring opportunities
- ❑ **Model development for event-based performance prediction**

Elizabeth Fassman-Beck, Ph.D.
Department Head, Engineering
elizabethfb@sccwrp.org

Danhui Xin, Ph.D.
Scientist, Chemistry
danhuix@sccwrp.org

Stay tuned and thank you!

SMC Kick-off!
Call for Advisory Group Members

Mechanistic Studies on Pollutant Removal by Stormwater BMPs

Elizabeth Fassman-Beck, Ph.D.

Engineering Department Head

Sept. 2024

Agenda

- ❑ Project Background
- ❑ Logistics
- ❑ SMC scope: modeling and field validation
- ❑ Call for advisory committee members

Background

- SMC Research Agenda 2019-2024 Project 3.1 Mechanistic Studies on Pollutant Removal by Stormwater BMPs

- 5th highest ranked project in the Research Agenda

- Project aims to quantify pollutant removal mechanisms, and develop a model that will aid in future BMP design and pollutant removal prediction at field scale.
  - BMP type: biofiltration
  - Removal mechanism: sorption
  - Pollutant types: dissolved copper and PFAS

Logistics

Phase I: Lab-based (2023-March 2025)

CALIFORNIA
Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

Lab experiments

Mechanistic model

Phase II: Field-based (July 2024-2026)

Southern California
STORMWATER MONITORING
Coalition

Field validation

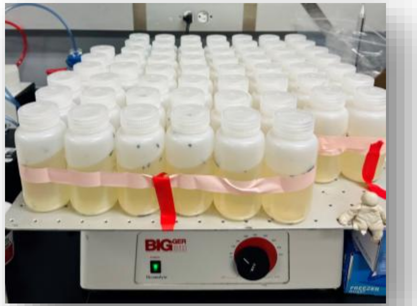
Phase 1: Lab-based

☑ **Media characterization**

Quantify properties of candidate media components:

- Cation exchange capacity
- BET surface area
- Etc.

☑ **Batch experiments**



Select media and determine ratios of materials to mix in columns:

- Sand
- Biochar
- Regenerated activated carbon
- Zeolite

☑ **Column experiments**

Measure Cu and PFAS removal by 4 different media mixtures. Establish breakthrough.

↻ **Initial model development**

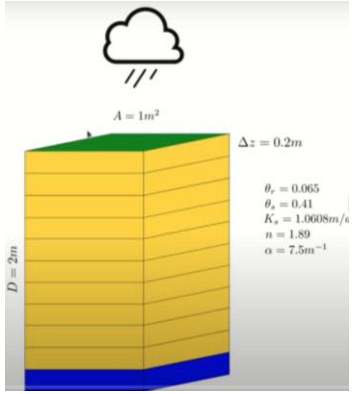
ELSEVIER

Environmental Modelling & Software

Volume 164, June 2023, 105707

An extensible, plugin-based tool for modeling flow and reactive transport in water systems

Arash Massoudieh [a], Khiem Nguyen [a], Sudhir Murthy [b]



OpenHydroQual

Phase 2: Modeling & Field Validation

Southern California
STORMWATER MONITORING
Coalition

Scope:

☐ Conduct field monitoring to generate data according to model needs

- Identify candidate BMPs. Construct if needed → ADVISORY COMMITTEE
- Sampling for dissolved copper & PFAS → BMP “owner”/SMC Member Agency & SCCWRP

☐ Adjust & validate model as-needed

- Develop success criteria → ADVISORY COMMITTEE

☐ Apply model for answering your future questions

- What do you want the model to do?? → ADVISORY COMMITTEE

Call for Advisory Committee Members

- One member per agency
- Suggestions for representatives
  - Does not need to be a modeler themselves
  - Quantitatively oriented
  - Familiar with BMP design and/or permitting/compliance
- Effort
  - Anticipate monthly meetings through the end of this year
- Send names/contacts to elizabethfb@sccwrp.org

Elizabeth Fassman-Beck, Ph.D.
Department Head, Engineering
elizabethfb@sccwrp.org

Danhui Xin, Ph.D.
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Edward Tiernan, Ph.D.
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Thank you!

APPENDIX F. 2024 CASQA CONFERENCE PRESENTATION

Appendix F

CASQA 2024 | October 21st | Session 1
Track: BMP and Control Measure Effectiveness Assessment

Media Cation Exchange Capacity (CEC) as a Predictor of Copper Sorption in Biofiltration

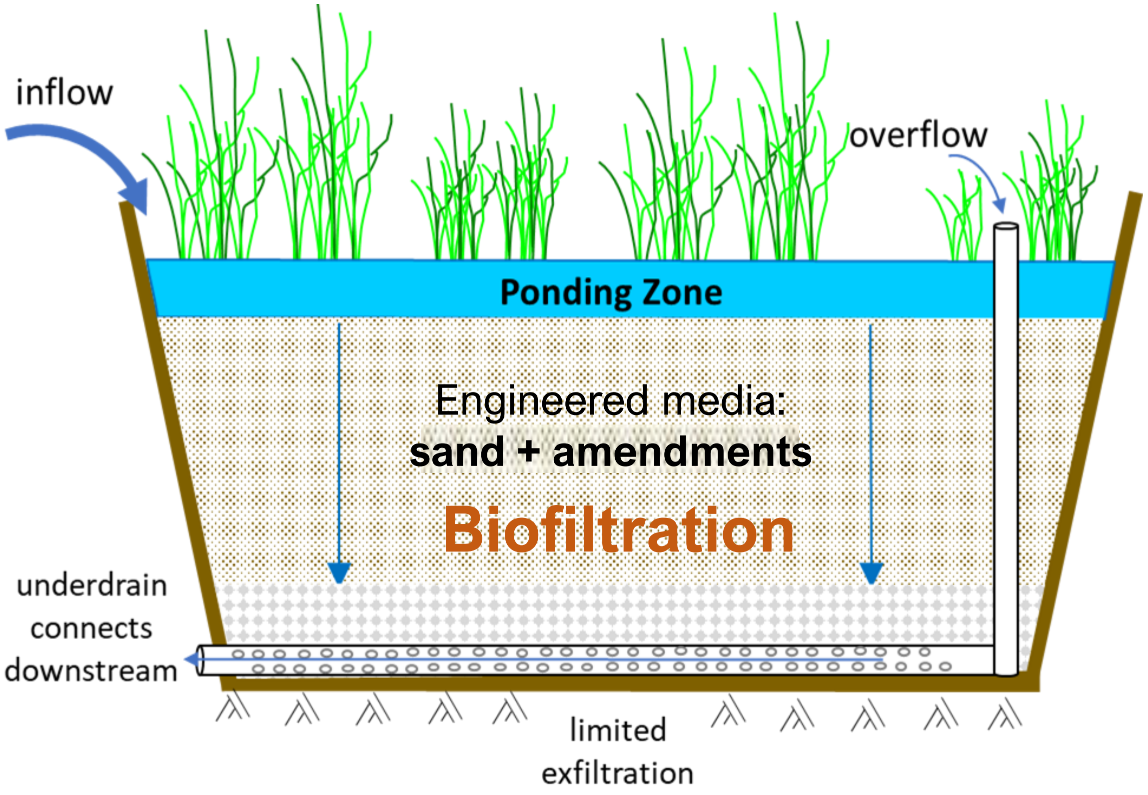
Danhui Xin, Ph.D. (presenter)[1], Elizabeth Fassman-Beck, Ph.D.[1], Allen P. Davis, Ph.D.[2]

[1] Southern California Coastal Water Research Project
[2] University of Maryland

Background

Key functions of biofiltration BMP

- Volume reduction (water quantity)
- **Pollutant removal (water quality)**
  - TMDL compliance
  - Engineered media

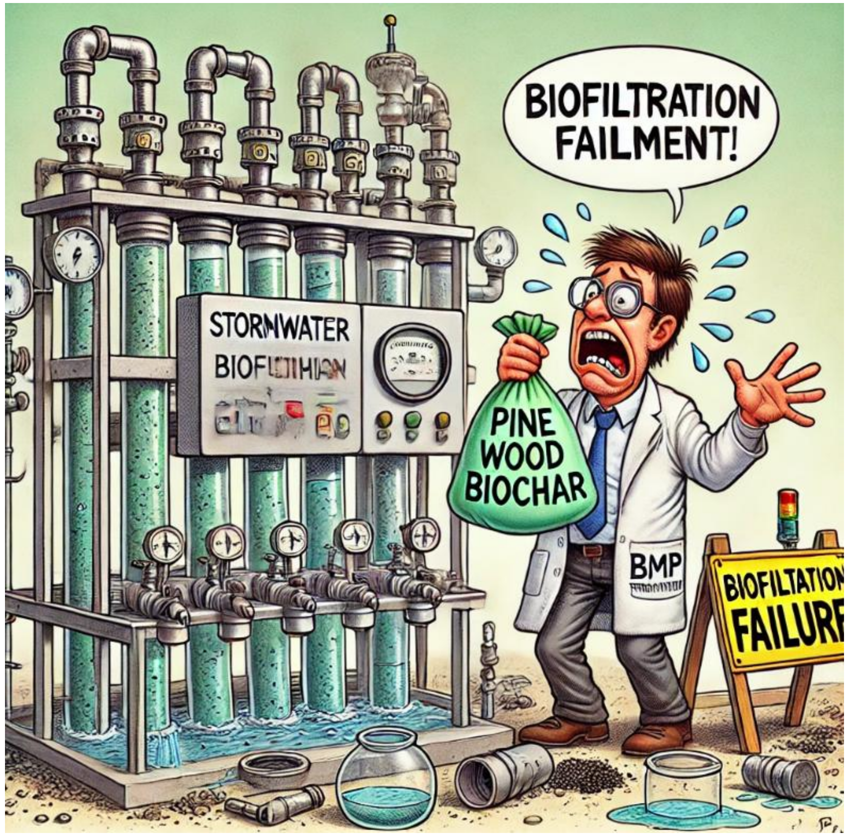


Variable and unpredicted water quality performance in biofiltration!

Background

- **BMP design guidance**
    - Design procedure based on water quantity
    - Rules-of-thumb for water quality
- **Black box approach**
    - Monitor influent and effluent
- **Industry focus on the media type**

Is "media type" reliable?



Goals

- BMP design guidance

  → Quantitative support for media design for water quality
- Black box approach

  → Unpack: Identify processes & mechanisms for pollutant removal
- Industry focus on the media type

  → Shift from “media type” to “media property”

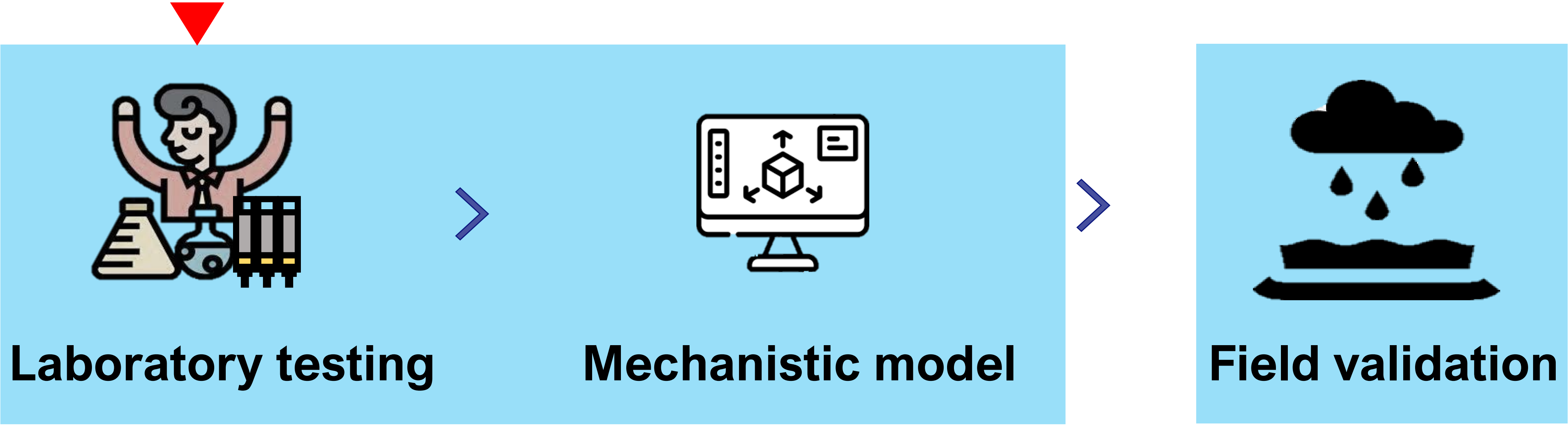
Objective

Target pollutant: Dissolved Cu

Removal mechanism: Sorption

Objective: Identify **measurable media properties** that can quantitatively predict dissolved Cu sorption in biofiltration.

Approach



Laboratory testing

Mechanistic model

Field validation

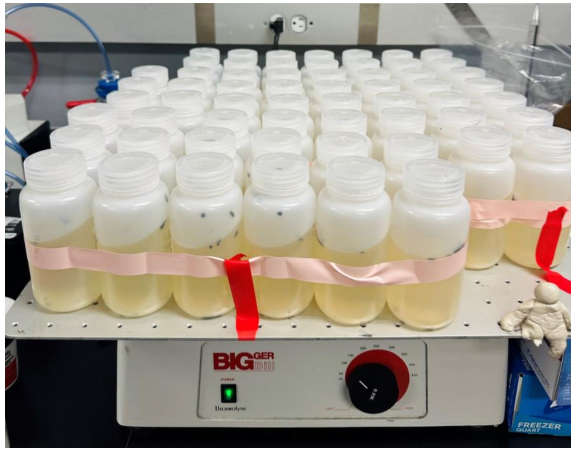
Laboratory testing

Measuring properties of media components ›

Testing Cu sorption to media in batch reactors ›

Validating findings in flow-through columns

Candidate media characterization



Batch experiments

Column experiments

Runoff for batch and column experiments

Create (close-to-real) runoff

Washing a parking lot using tap water

Collect runoff (background matrix)

Spike dissolved Cu

Engineered media

Selection criteria:

- Available at scale
- Suitable size fraction

sand (ASTM C33)

Pacific Aggregates (PA)

+

amendment alternatives:

clinoptilolite Zeolite

regenerated activated carbon (RAC)

biochars:

- **Rogue**
- **Hydrophobic**
- **Hydrophilic**

Characterization of candidate media components

design guidance

sorption–related properties

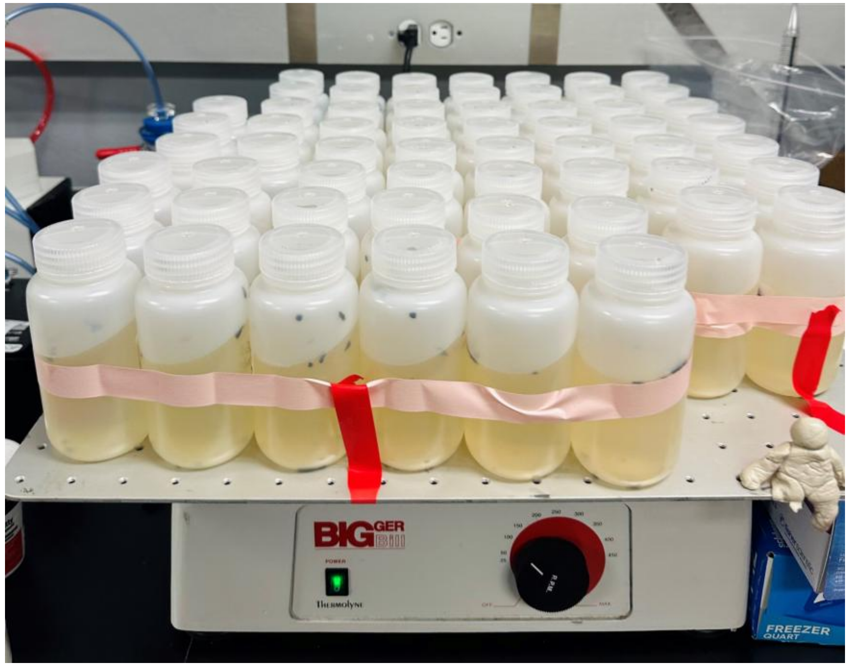
Media	**Bulk density**	**pH**	**Loss on Ignition (LoI)**	**NO_3^--N**	**Olsen-P**	**CEC_{Ba}**	**CEC_X**	**Contact angle**	**SSA_{BET}**
	(g/cm^3)		(% weight)	(mg/kg)		(meq/100g)		(°)	(m^2/g)
PA sand	1.65	7.94±0.00	0.13	1.5	<20	<2.0	2.1	53.6±9.6	0.02
Zeolite	0.88	9.61±0.03	3.8	20.0	<20	7.6	28.3	62.6±10.3	15.16
RAC	0.55	9.10±0.57	1.4	2.2	424	3.6	5.5	71.9±9.4	840.50
Rogue biochar	0.12	9.58±0.04	74.6	0.8	1324	15.0	25.3	54.6±14.7	546.51
Hydrophobic biochar	0.17	7.75±0.07	66.4	2.2	292	13.7	7.7	77.4±9.7	237.05
Hydrophilic biochar	0.16	5.99±0.10	53.4	20.0	1232	21.0	19.8	73.4±7.6	443.62

Batch Cu sorption experiments

- Known initial Cu concentration
- Known amount of media

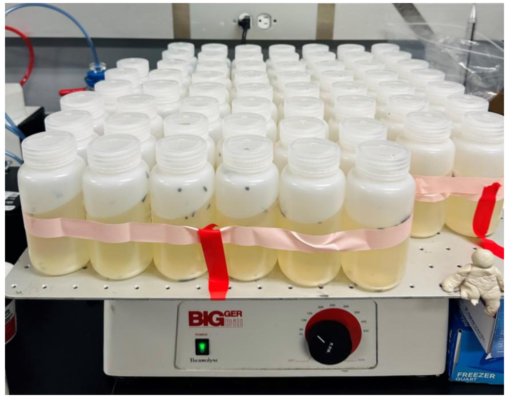
→ Mix for 72 h

- Measure remaining Cu concentration
- Sorbed Cu
    - initial - remaining

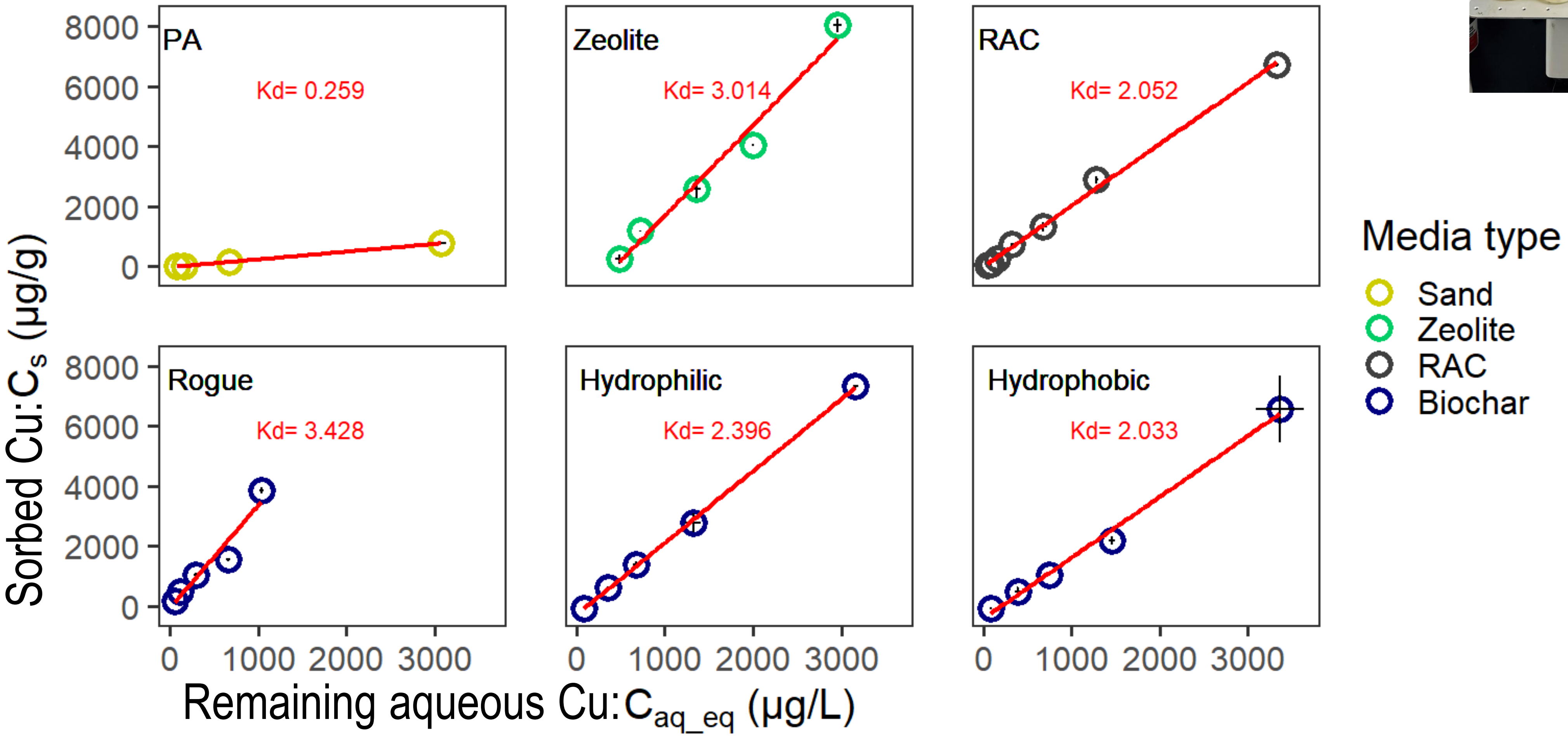


Batch sorption experiments

Batch Cu sorption experiments

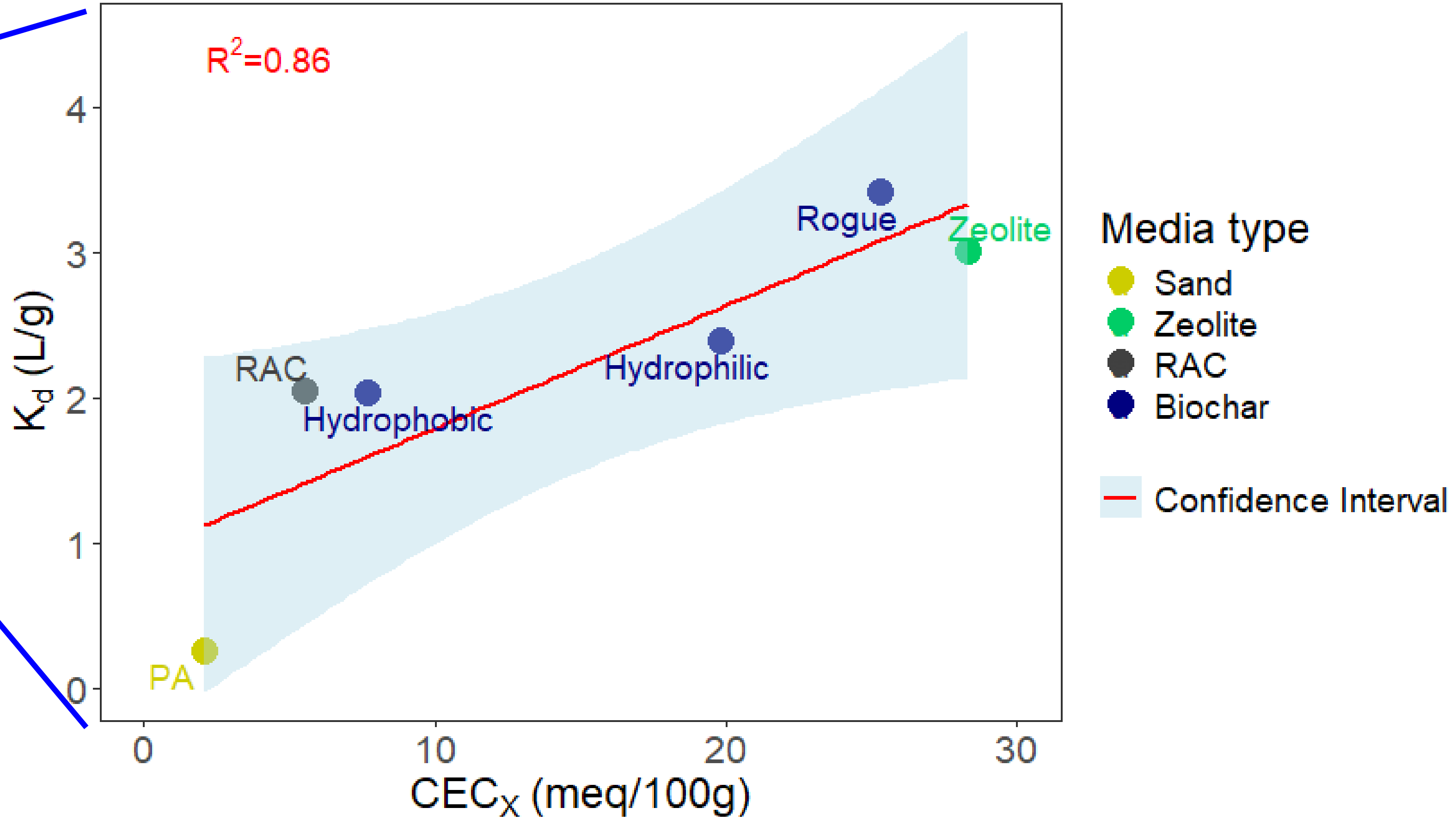


Slope K_d(L/g)



Slope (K_d) vs. Media properties

	R^2
CEC_X	0.86
CEC_{Ba}	0.55
LoI	0.49
pH	0.37
SSA_{BET}	0.34
Contact angle	0.11

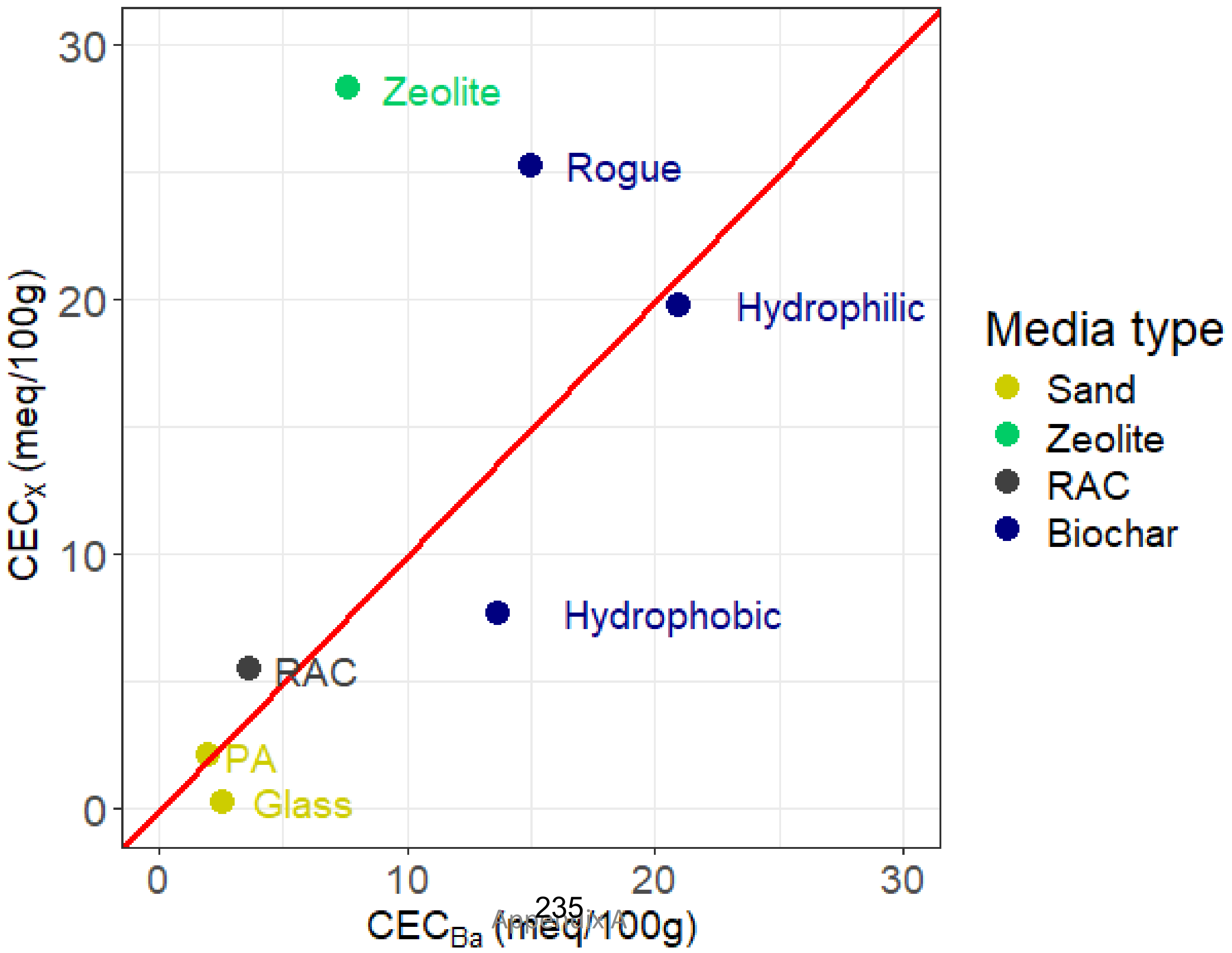


Media CEC_X can predict Cu sorption in a batch system.

Use CEC_X (measured from exchangeable cationic nutrients K^+, Na^+, Ca^{2+}, Mg^{2+})

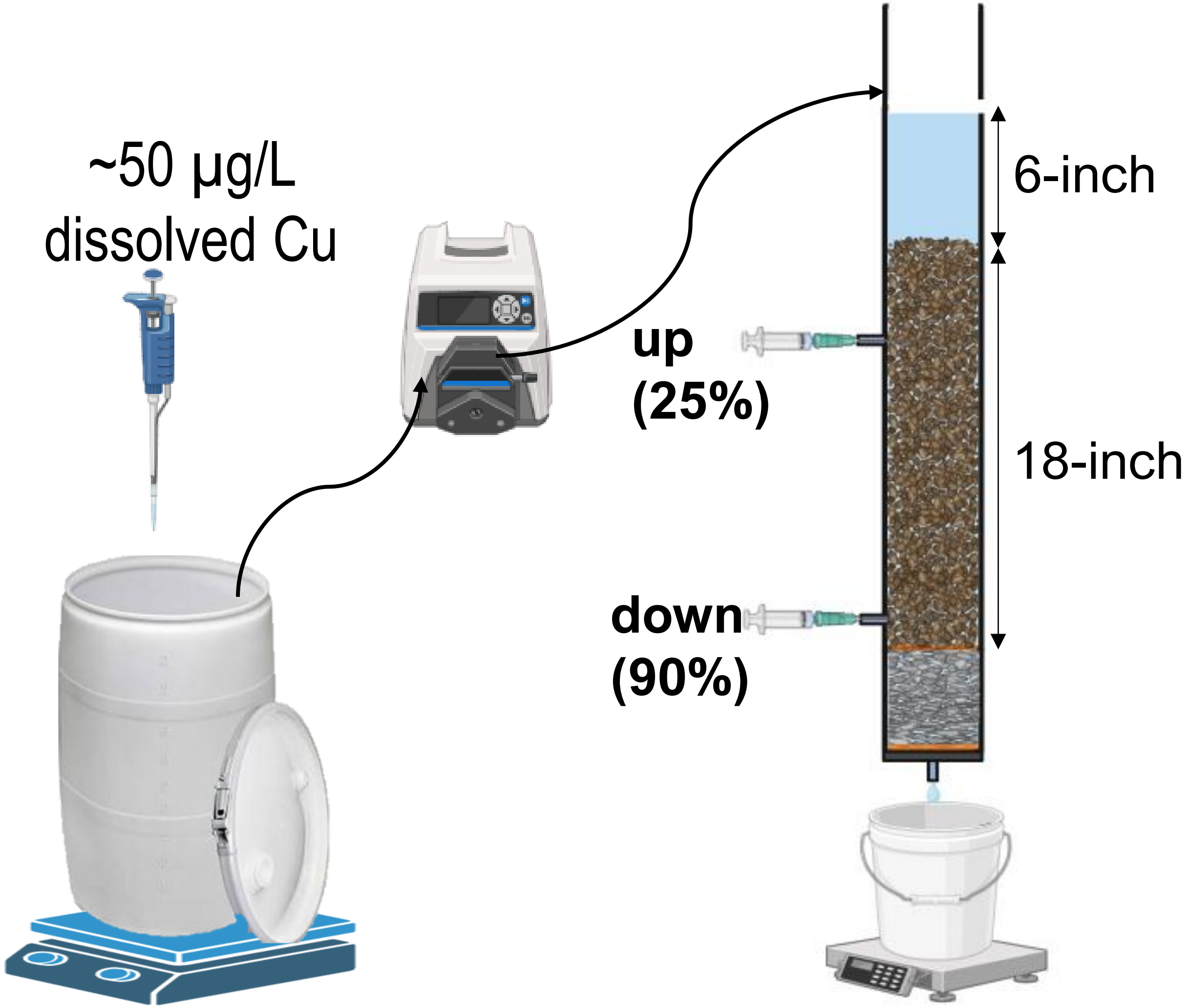
	R^2
CEC_X	0.86
CEC_{Ba}	0.55
LoI	0.49
pH	0.37
SSA_{BET}	0.34
Contact angle	0.11

Design guidance does not specify testing methods.

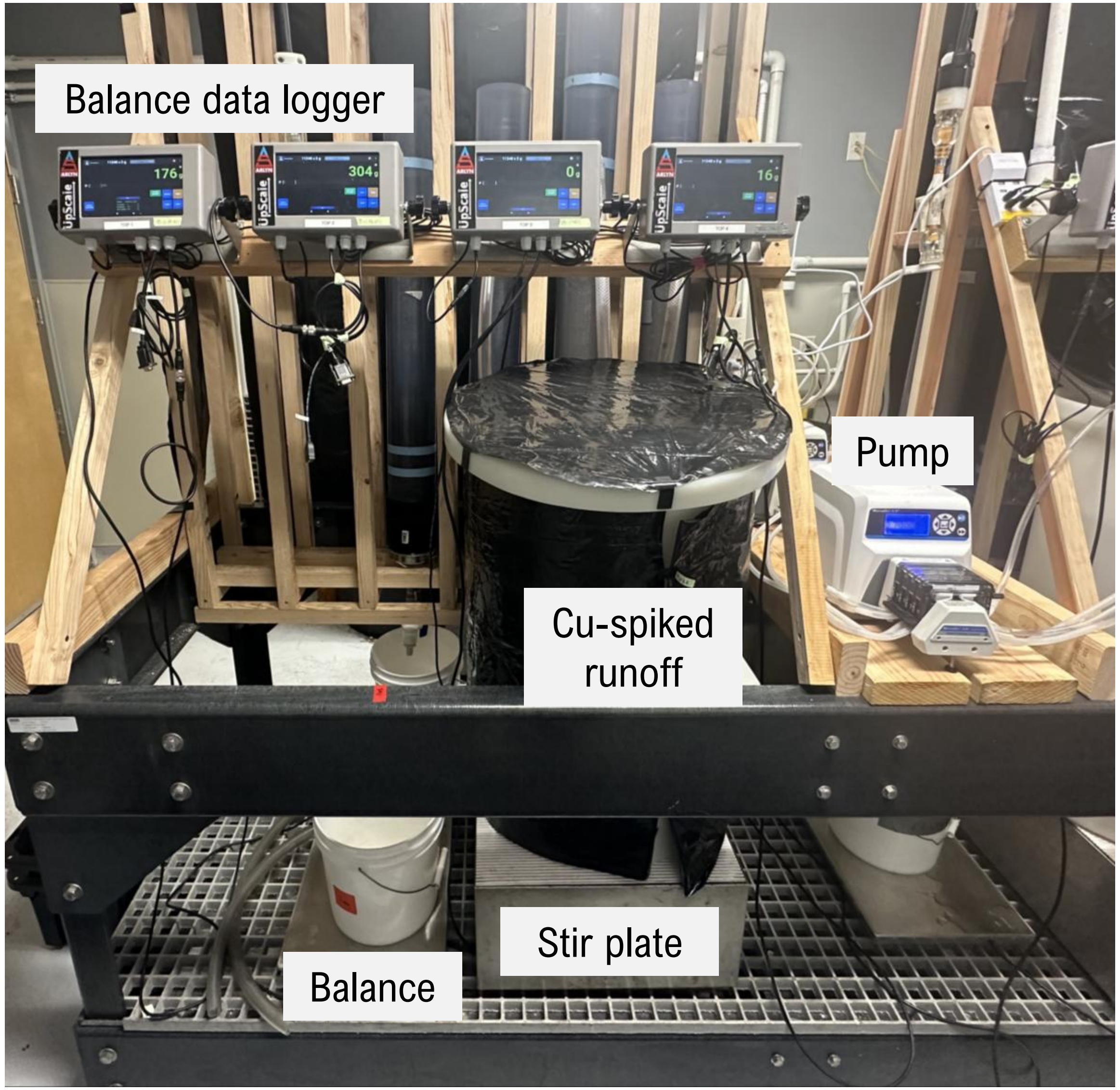


Flow-through column experiments

- 18-inch media layer
- 6-inch ponding depth
  - Infiltration rates were monitored daily (20-80 in/h)
- Sampling for dissolved Cu
  - Influent
  - Down effluent: concentrations
  - Up effluent: media capacity



Flow-through column experiments



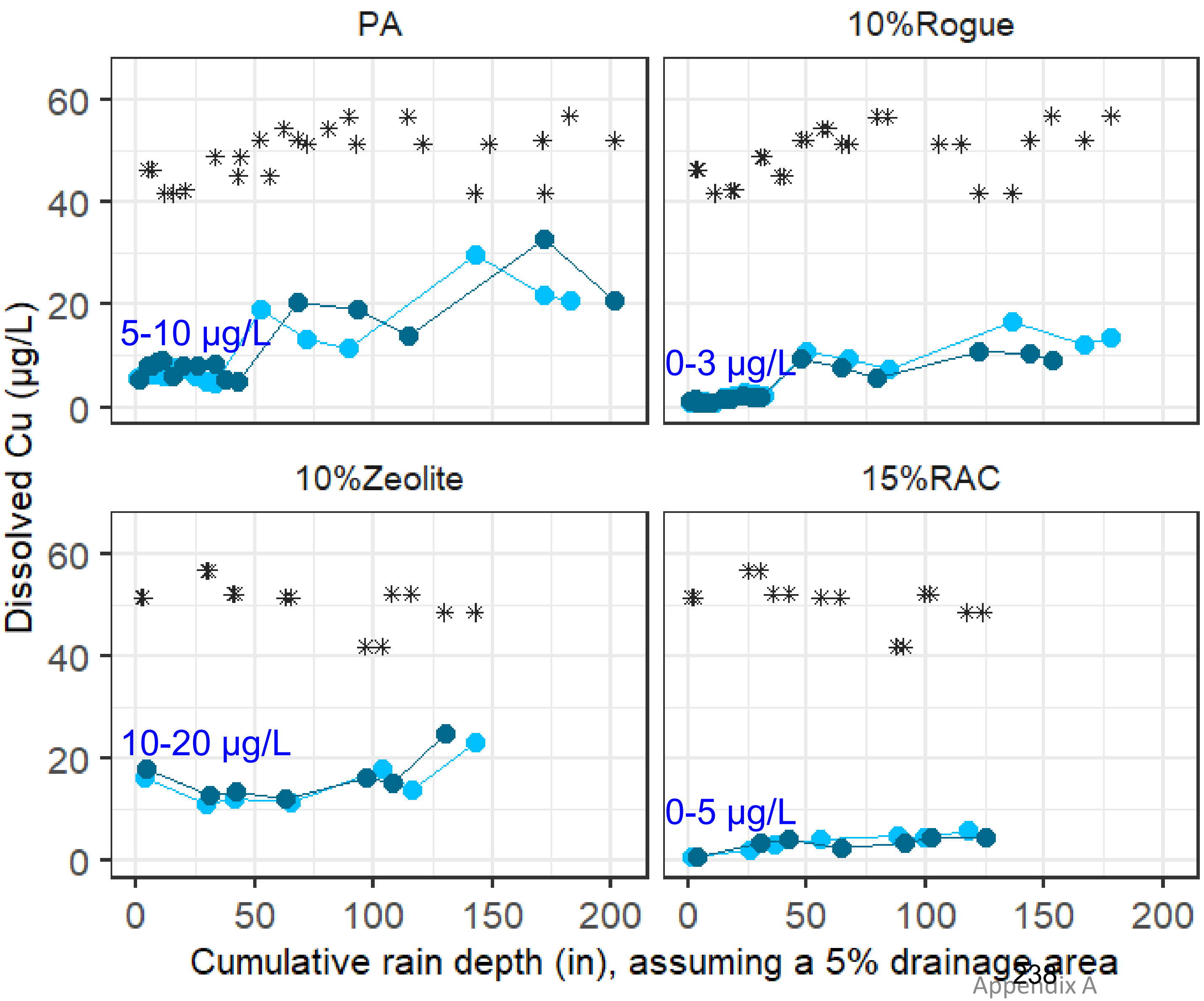
4 media mixes (duplicates)

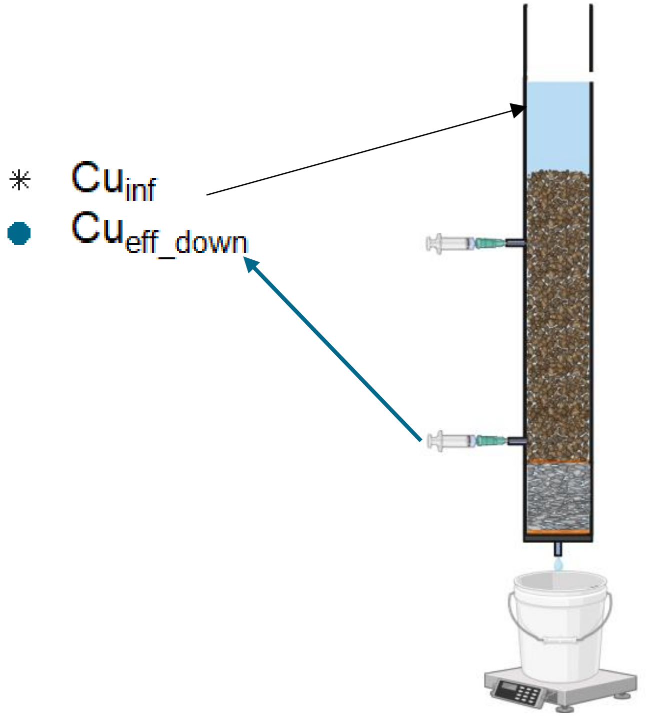
- PA sand only
- 10% Rogue + PA
- 10% Zeolite + PA
- 15% RAC + PA

Operated 2-3 days a week over 5 months (up to **900 L** runoff for each column, representing 200-in of cumulative rain)

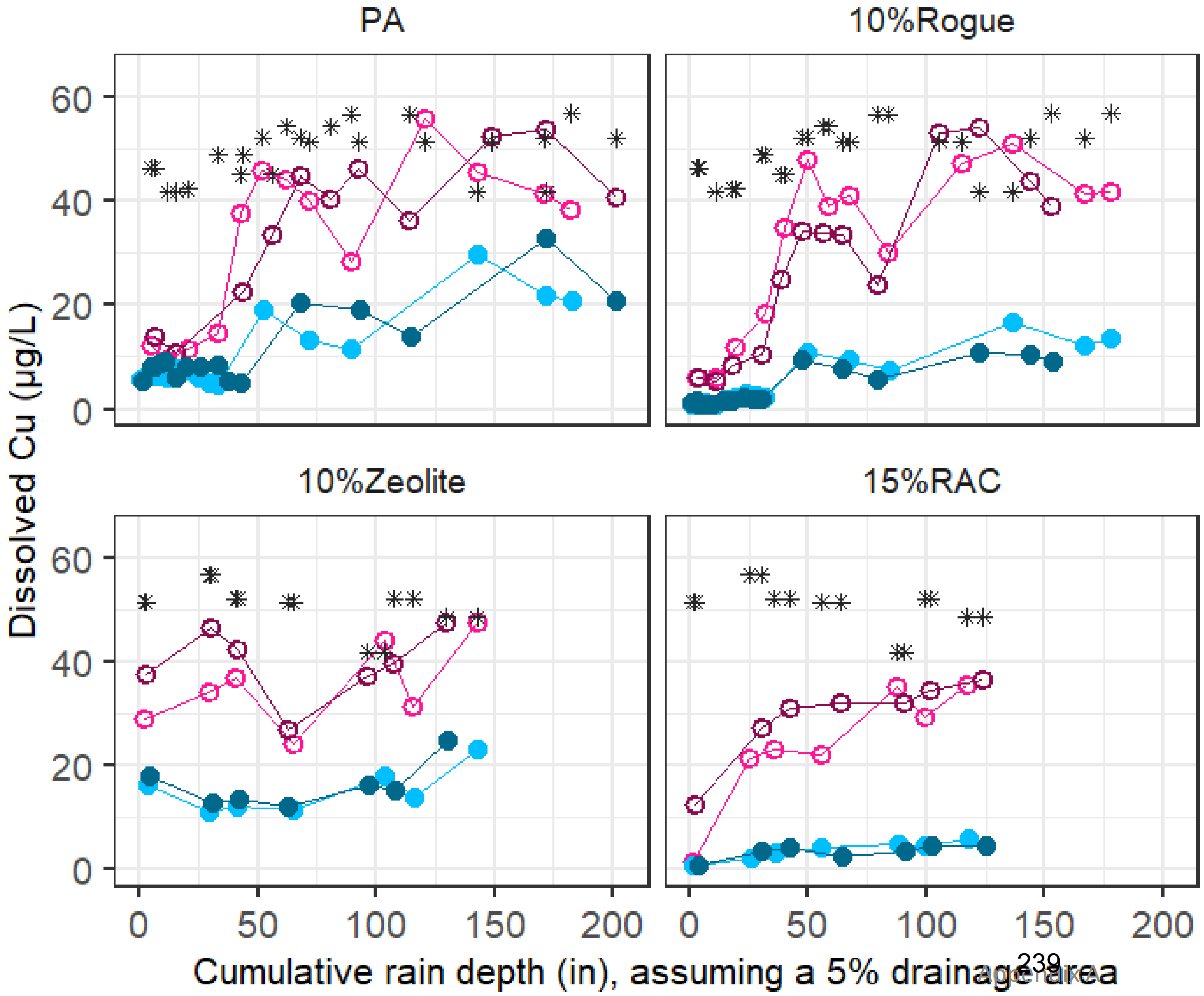
Does treatment differ?

- 200 in: 20 years (10 in/year)
- Initial Cu_{eff}

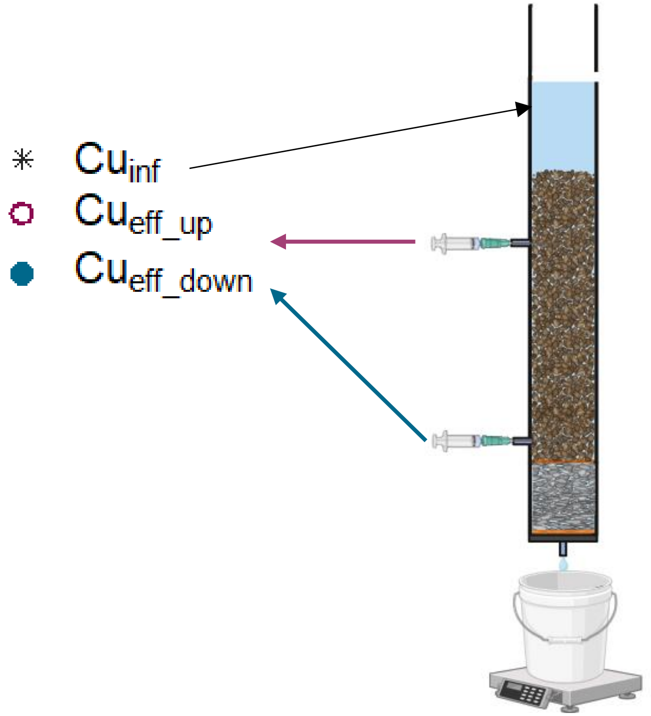




Does capacity differ?

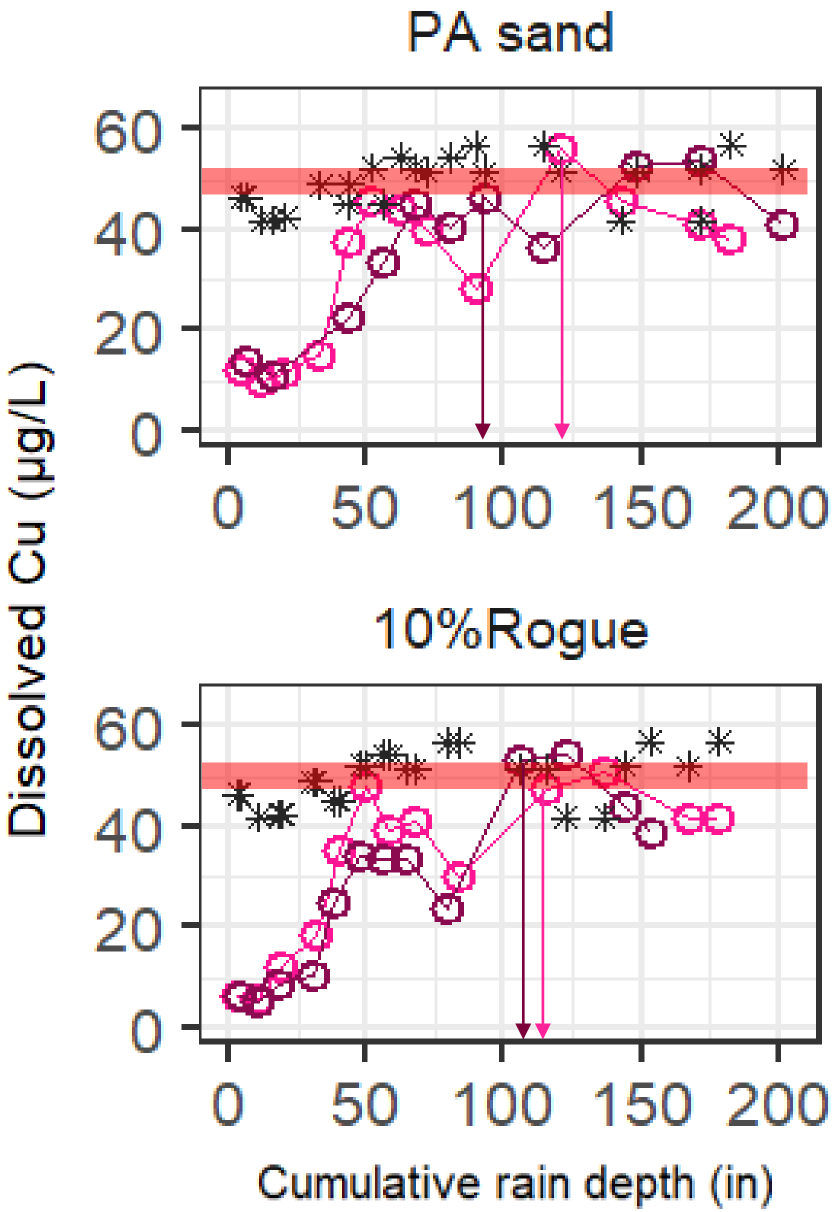


- Breakthrough
  - $Cu_{eff} = Cu_{inf}$



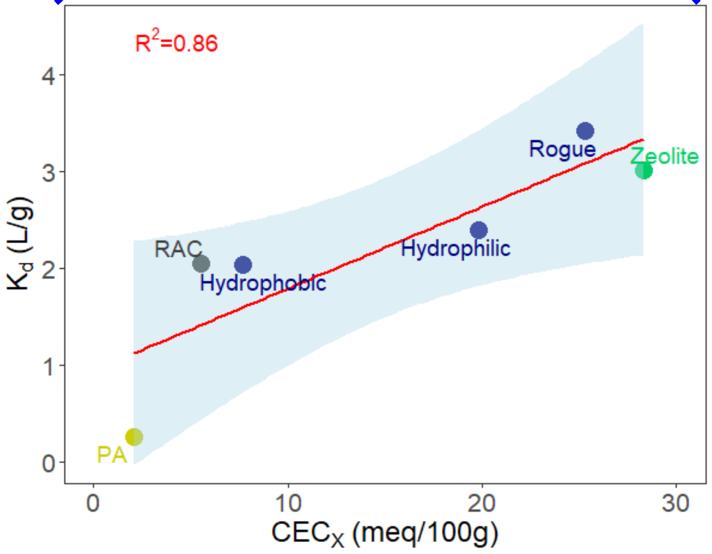
Breakthrough

- Breakthrough
  - After similar amount of runoff



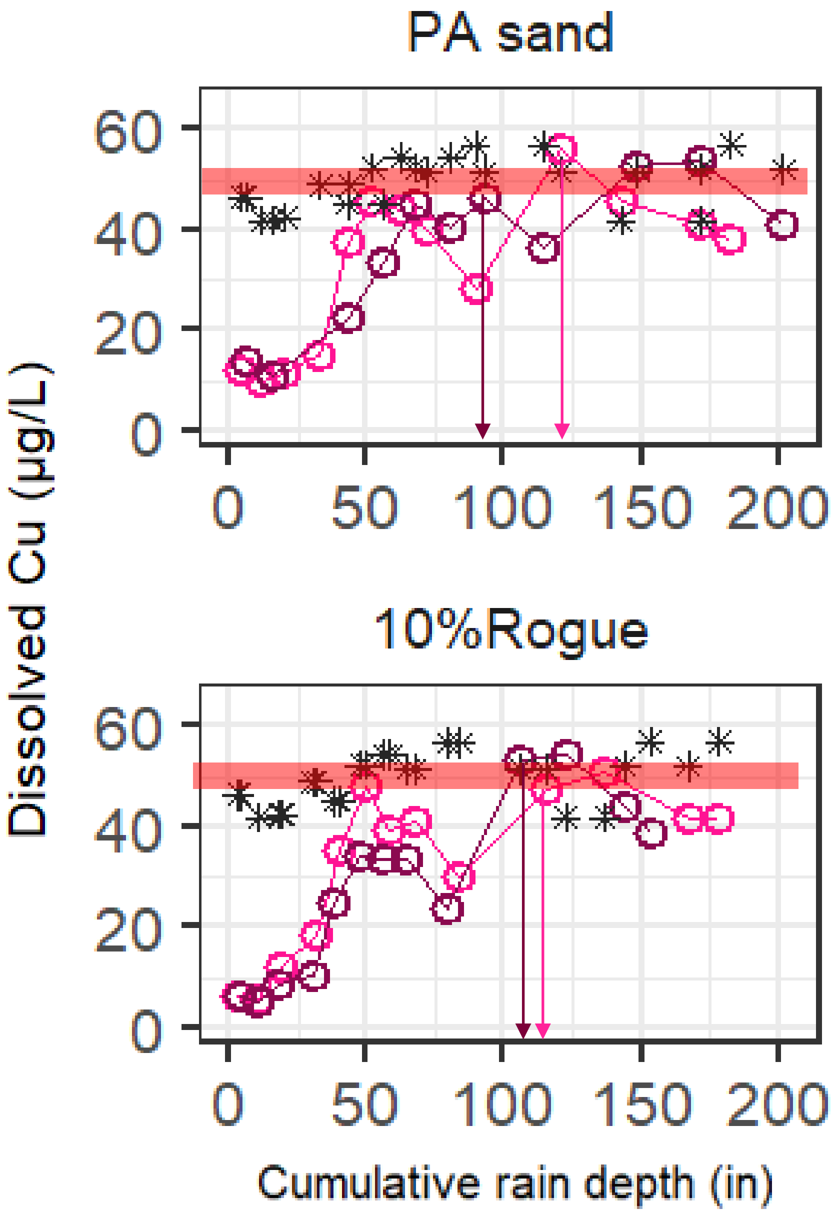
	CEC$_X$	K$_d$	Cu$_{inf}$	Cu sorption capacity
	meq/100g	L/g	µg/L	**µg Cu/g**
PA	2.1	0.27	49	13
Rogue	25.3	3.24	49	156

By Mass



Appendix A

Can we predict breakthrough?



$$\text{volume (L)} = \frac{\text{Cu sorption capacity } (\mu g)}{Cu_{inf}\ (\mu g/L)}$$

PA	Cu sorption capacity	Media Volume	Media Volume	Media Cu sorption capacity	Breakthrough runoff volume	Breakthrough rain depth
	µg Cu/L	%	L	µg Cu	L	in
PA	21167	**100**	0.93	21608	409	**99**
Rogue		**0**				

10% Rogue	Cu sorption capacity	Media Volume	Media Volume	Media Cu sorption capacity	Breakthrough runoff volume	Breakthrough rain depth
	µg Cu/L	%	L	µg Cu	L	in
PA	21167	**90**	0.93	19440	404	**98**
Rogue	18527	**10**				

Take-aways

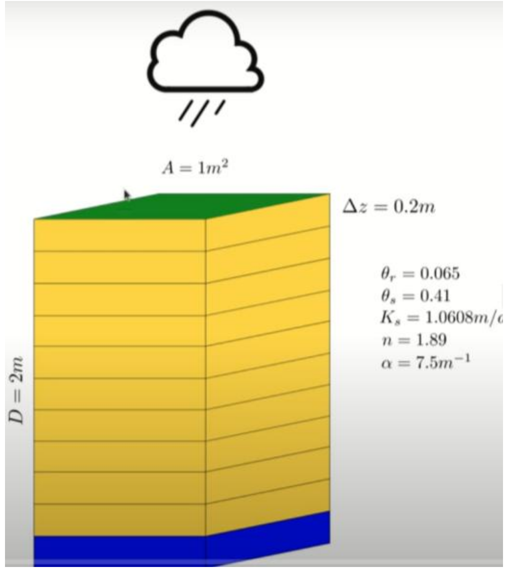
- CEC_X can serve as a design parameter for estimating the capacity (or lifetime) of biofiltration media for Cu.
    - Sand with a CEC_X can remove Cu.
    - Sand with amendments results in lower effluent concentrations.

- Shifting the focus from “media type” to “media property”.
    - Predictable performance.
    - Expand media choices.

Next steps

Laboratory testing

OpenHydroQual



Mechanistic model

A potential site: Riverside Flood Control

Field validation

For more information:
Danhui Xin, Ph.D.
danhuix@sccwrp.org

Thank you!

Stay tuned for CASQA 2025!

APPENDIX G. 2025 NATIONAL MONITORING CONFERENCE

Appendix G

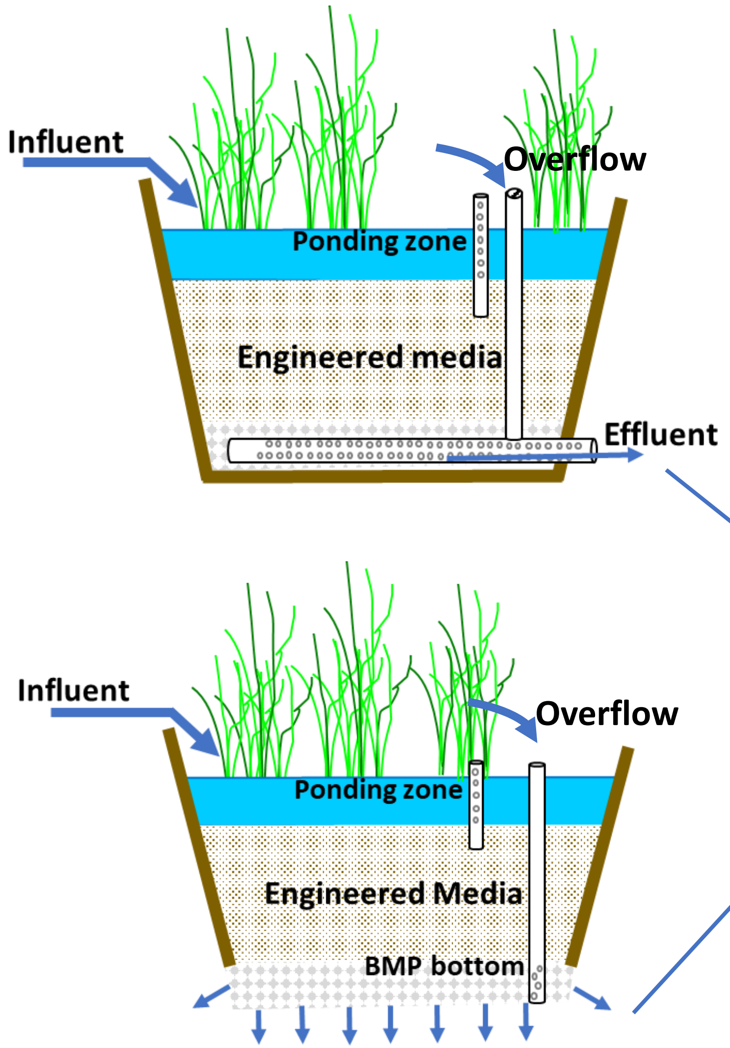
NWQMC 2025 | March
S24: Emerging Contaminant Transport and Fate in Green Stormwater Infrastructure

Effect of engineered media properties on Cu and PFAS treatment in biofiltration columns

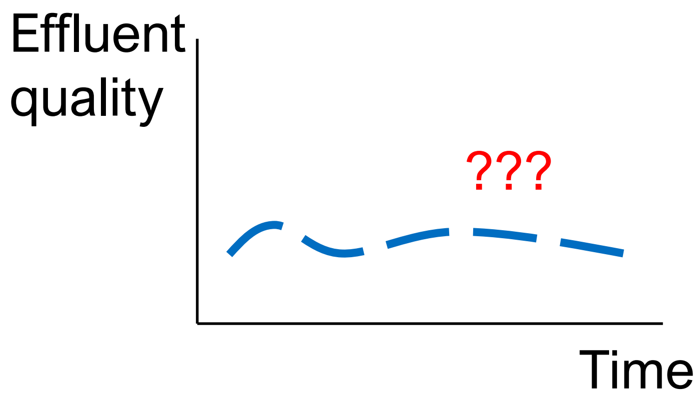
Danhui Xin, Ph.D. (presenter)[1], Elizabeth Fassman-Beck, Ph.D.[1], Allen P. Davis, Ph.D.[2]

[1] Southern California Coastal Water Research Project
[2] University of Maryland

Biofiltration (or bioretention)



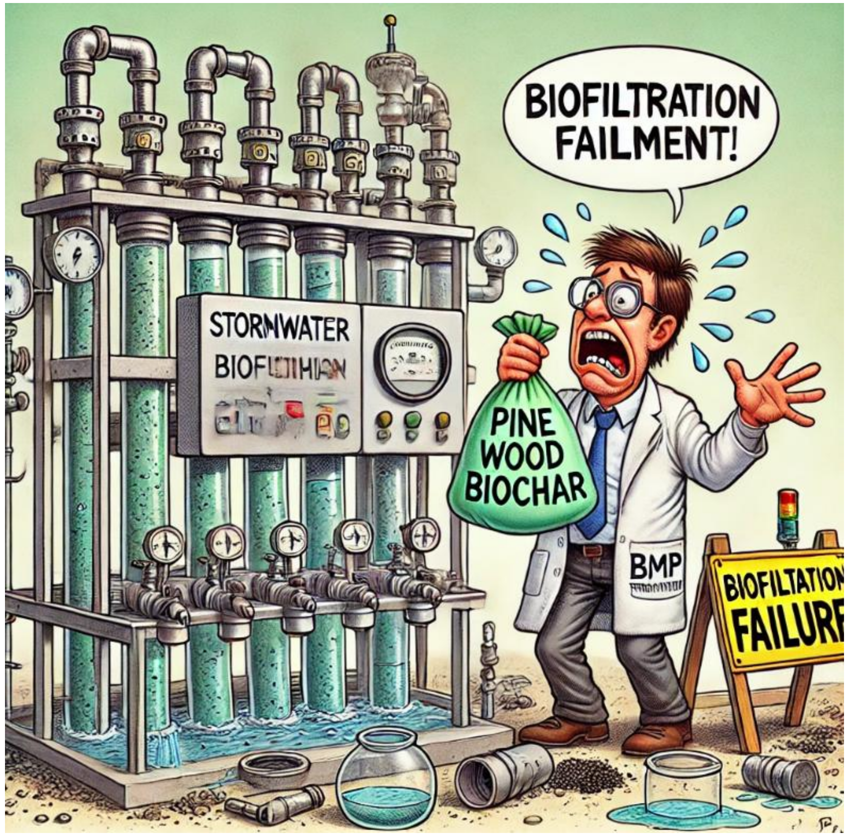
Key function: contaminant removal



Concerns for water quality

- **BMP design guidance**
  - Rules-of-thumb
    - 60-80% sand + topsoil/compost/amendments
  - Media testing parameters
    - Not designed to improve water quality
    - Rare field validation of parameters
- **Engineered media: sand + amendments**
  - Focuses on the amendment type

Is amendment “type” reliable?



Goals

- **Shift from “media type” to “media property”**
- **Provide quantitative support for BMP design guidance**

Objective: Identify **measurable media properties** that can predict **contaminant treatment** in biofiltration.

Targets

- **Dissolved contaminants**
  - Dissolved Cu – understudied
  - PFAS (PFOA and PFOS) – the first of its kind biofiltration column study
- **Removal mechanism**
  - Sorption

Engineered media: sand + amendment(s)

Sand (ASTM C33)

Pacific Aggregates (PA)

+

Amendment alternatives:

Zeolite

Regenerated
activated carbon
(RAC)

Biochars:
- Rogue
- Hydrophobic
- Hydrophilic

Controlled laboratory experiments

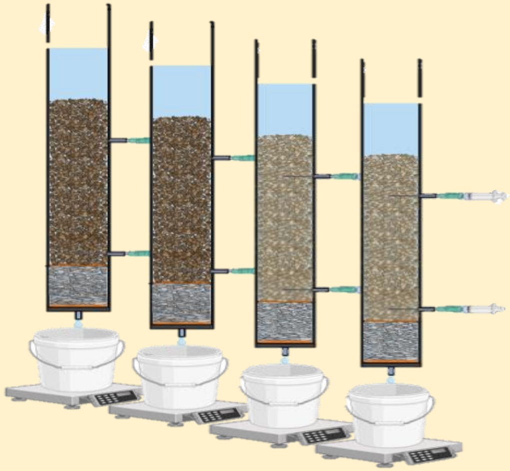
Batch experiments

dissolved Cu

Measure **sorption affinity (K_d)** of dissolved Cu to each media

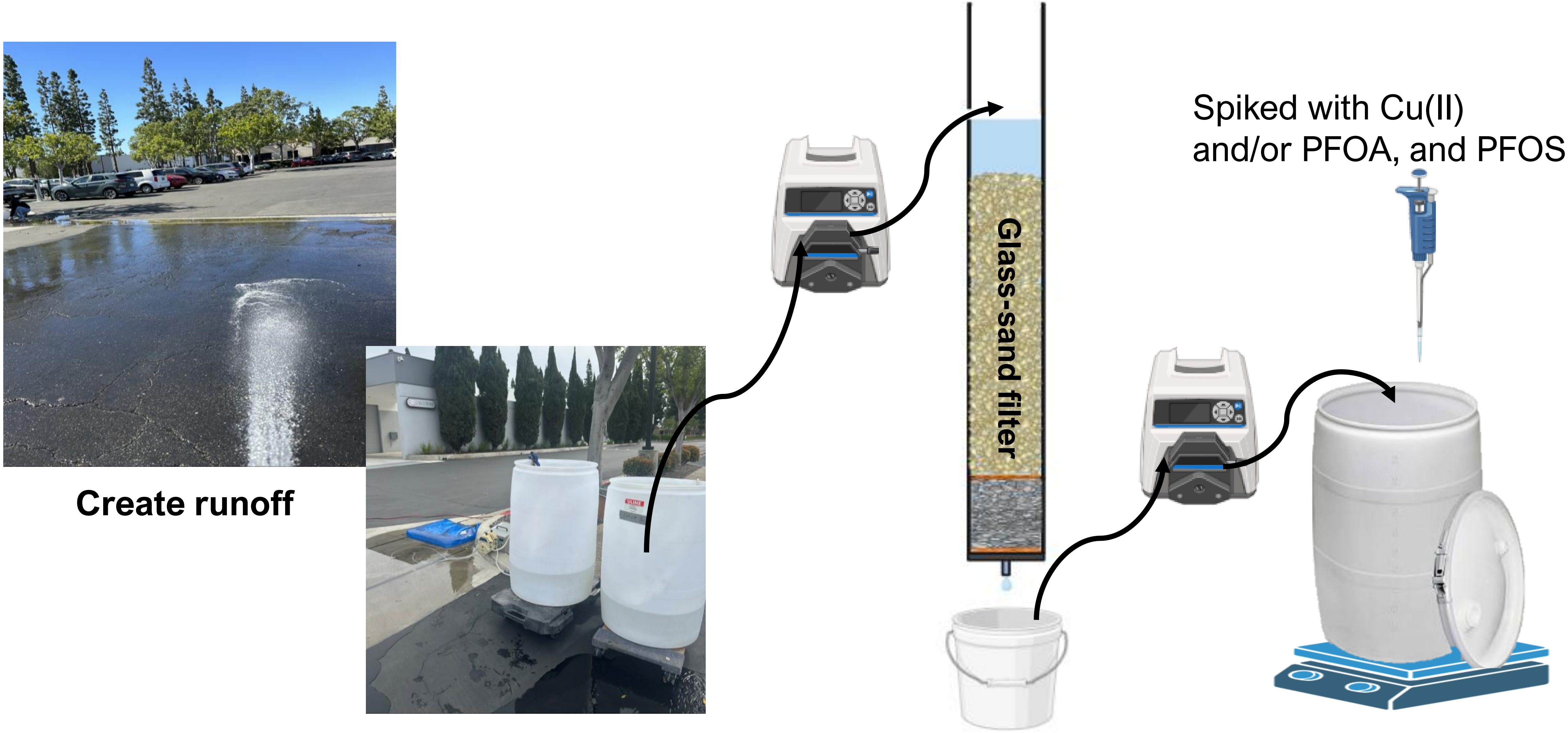
Column experiments

dissolved Cu and PFAS



Measure **effluent concentrations** over time and determine **sorption capacity**

Close-to-real runoff



Spiked with Cu(II) and/or PFOA, and PFOS

Create runoff

Background runoff

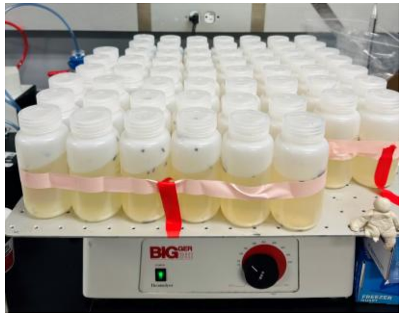
Pre-filtered runoff

Spiked runoff

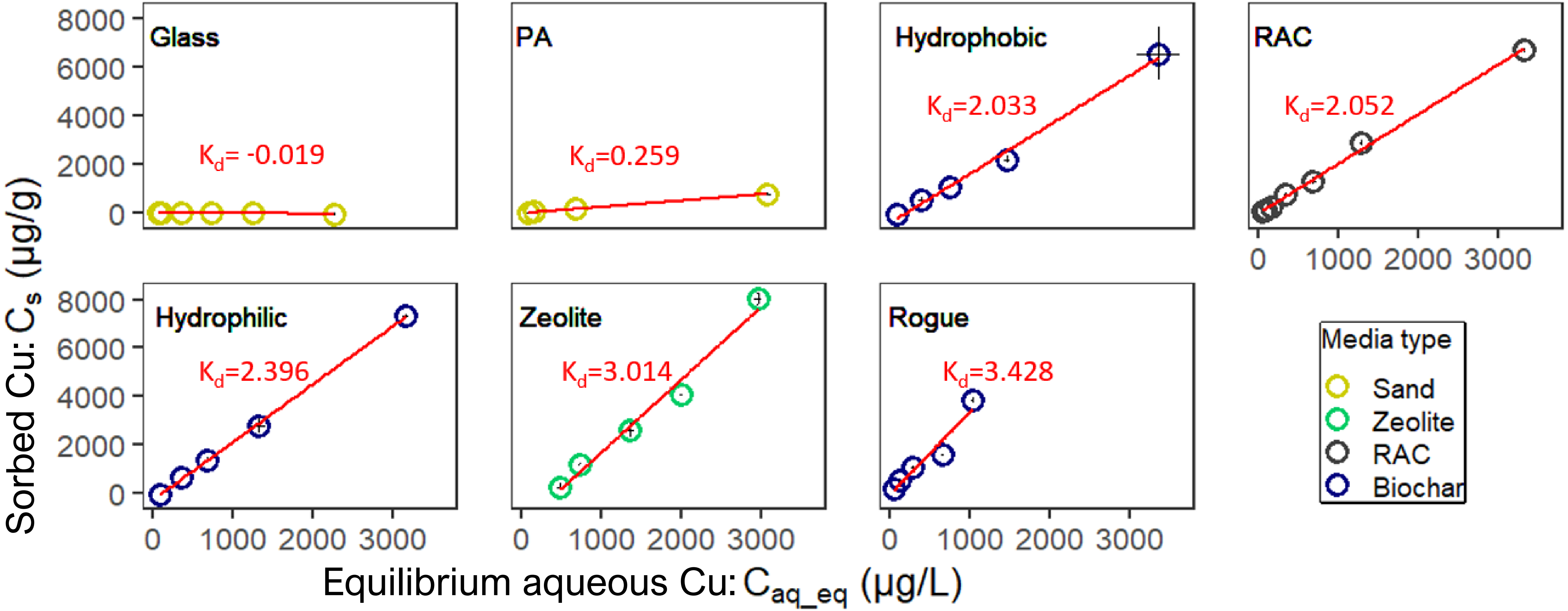
Characterization of candidate media

Media	Bulk density	pH	CEC_{Ba}	CEC_X	Contact angle	SSA_{BET}
	(g/cm^3)		(meq/100g)		(°)	(m^2/g)
PA sand	1.65	7.94	<2.0	2.1	53.6	0.02
Zeolite	0.88	9.61	7.6	28.3	62.6	15.16
RAC	0.55	9.10	3.6	5.5	71.9	840.50
Rogue biochar	0.12	9.58	15.0	25.3	54.6	546.51
Hydrophobic biochar	0.17	7.75	13.7	7.7	77.4	237.05
Hydrophilic biochar	0.16	5.99	21.0	19.8	73.4	443.62

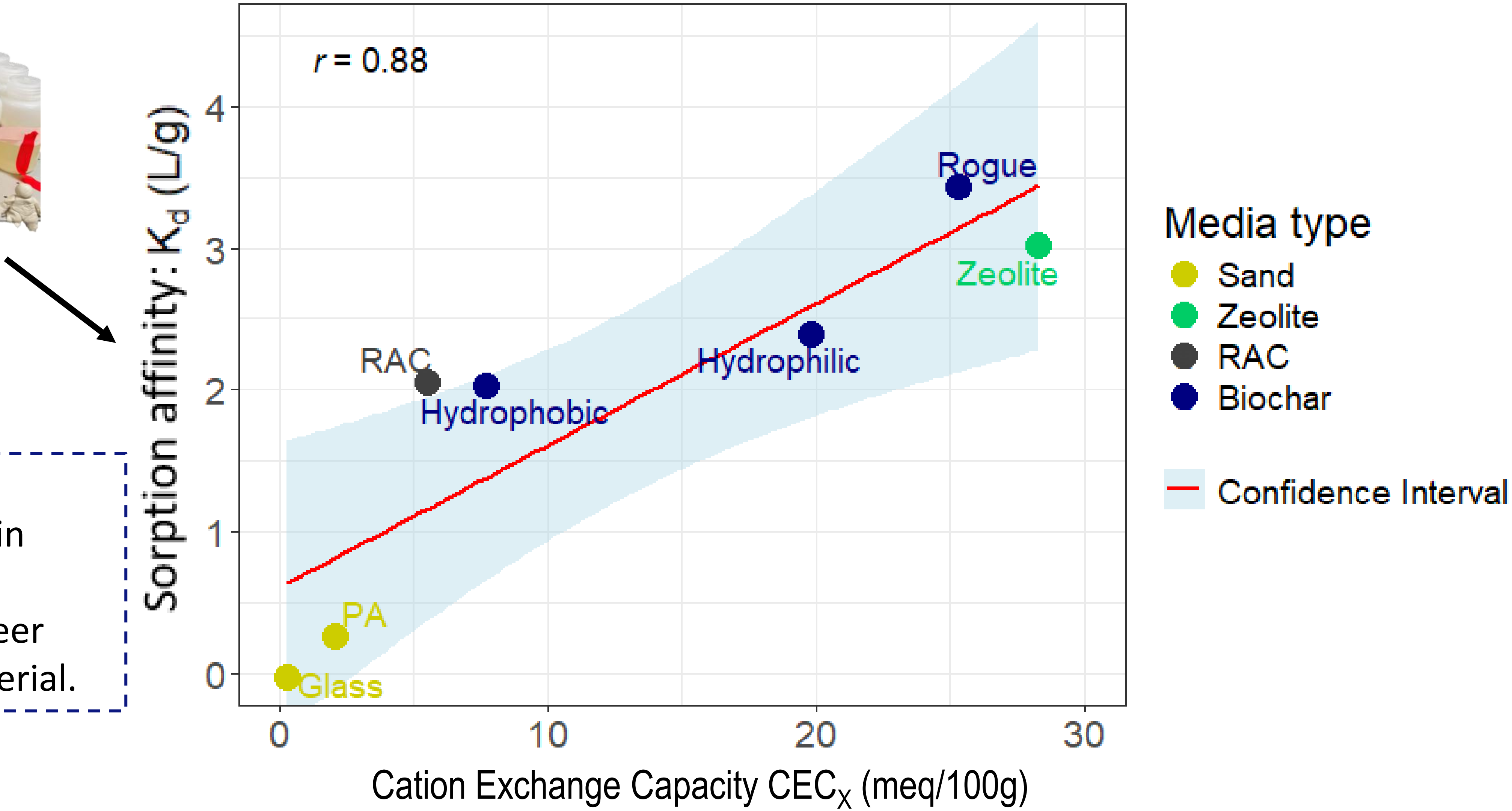
Batch sorption experiments (Cu only)



Slope= sorption affinity $K_d(\mathrm{L/g})$



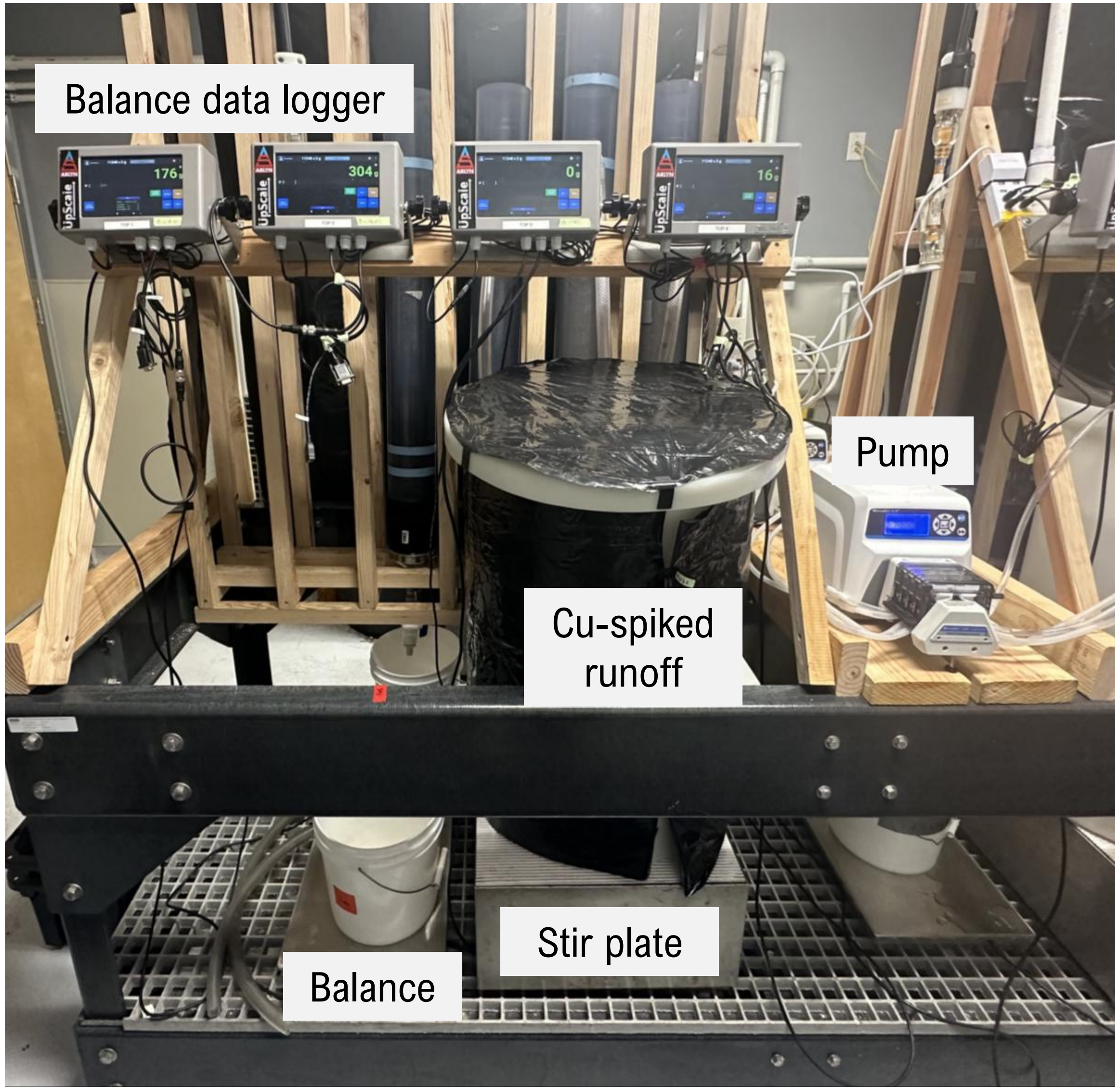
CEC$_X$ predicts Cu sorption



Practical Application:

- CEC$_x$ can be tested in advance.
- Helps design engineer select the best material.

Flow-through column experiments

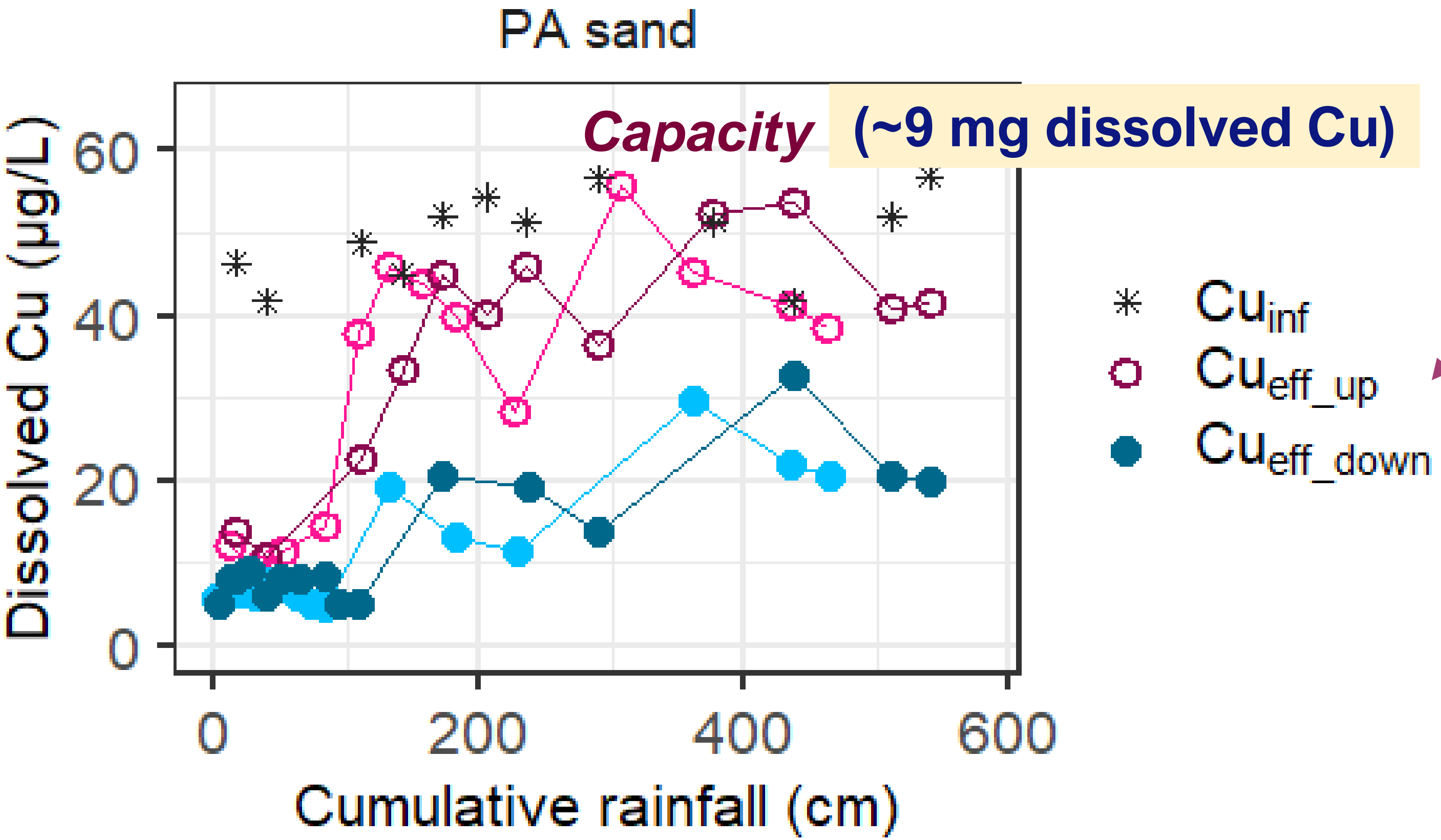


Four media mixes (duplicates)

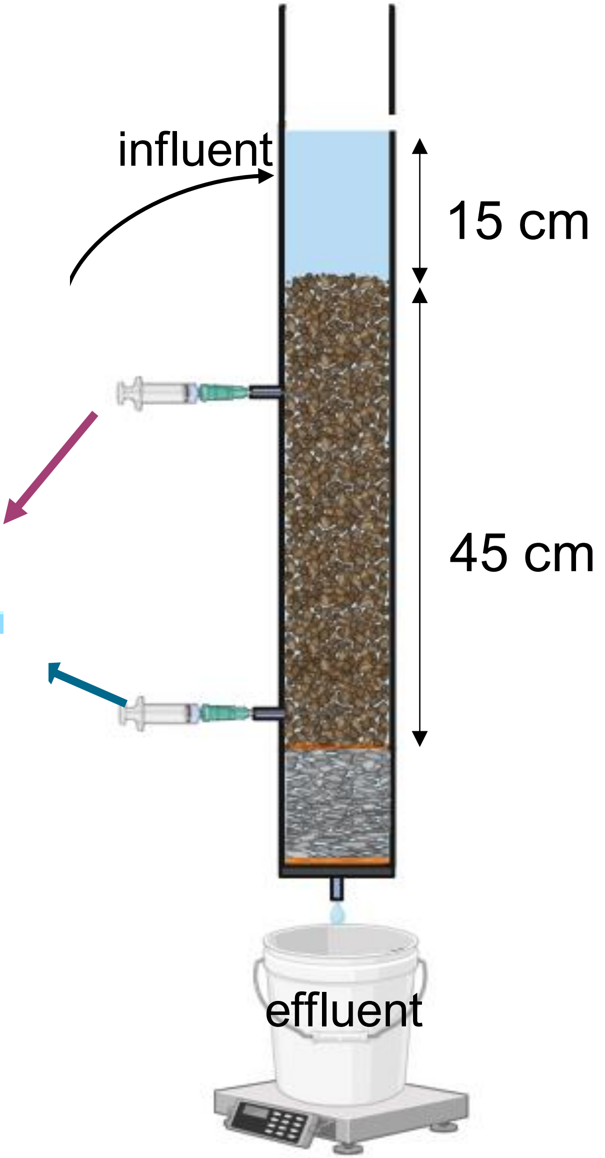
- PA sand only
- 10% Rogue + PA
- 10% Zeolite + PA
- 15% RAC + PA

Operated 2-3 days a week over 5 months (up to **900 L** runoff for each column)

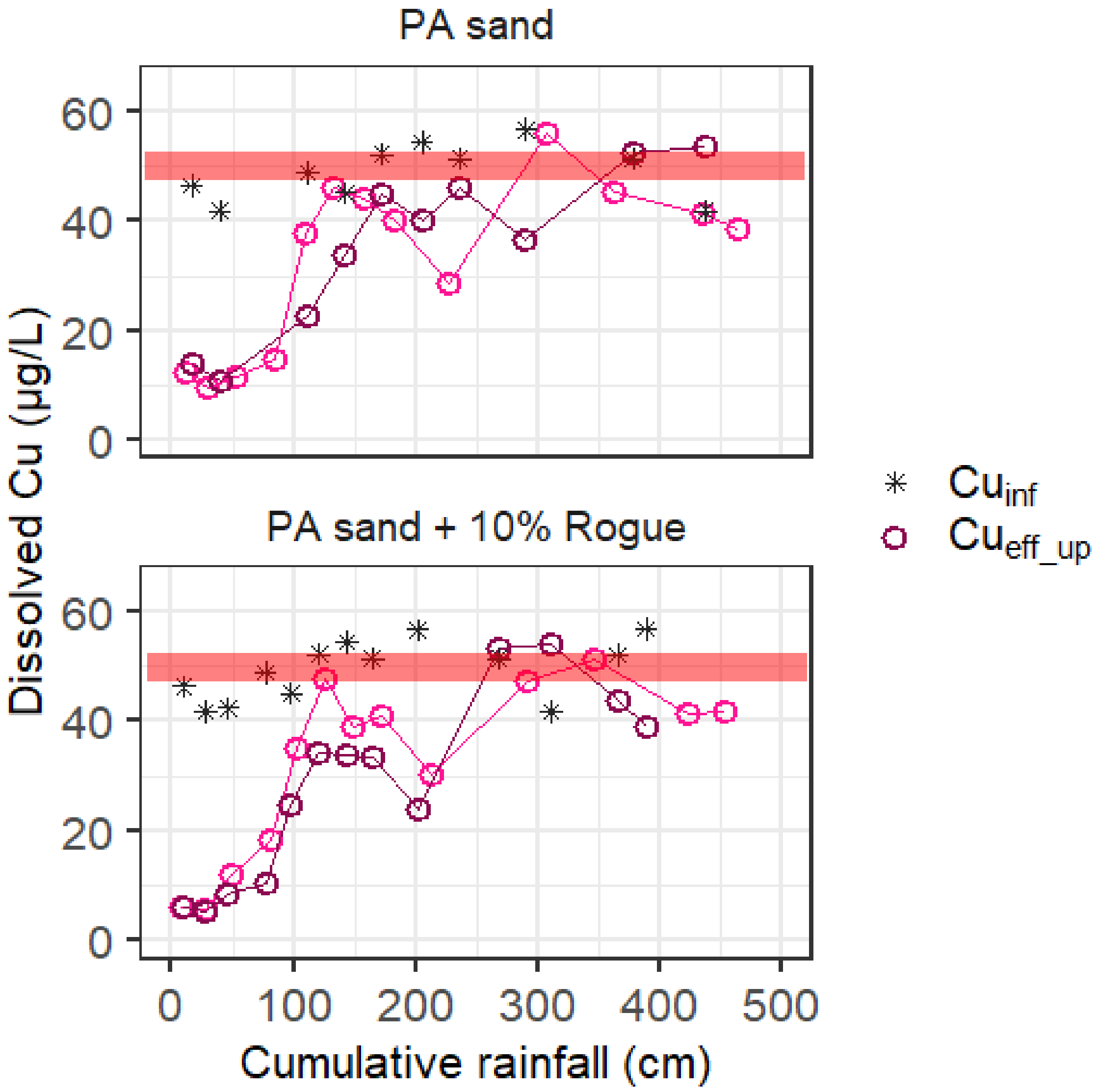
How much treatment occurred over time?



Capacity **(~9 mg dissolved Cu)**



Volumetric K_d to inform Cu sorption capacity



Both columns sorbed ~9 mg dissolved Cu

	Sorption K_d (L/g)
PA	0.26
Rogue	3.43

×

Bulk density ρ (g/L)
1646
119

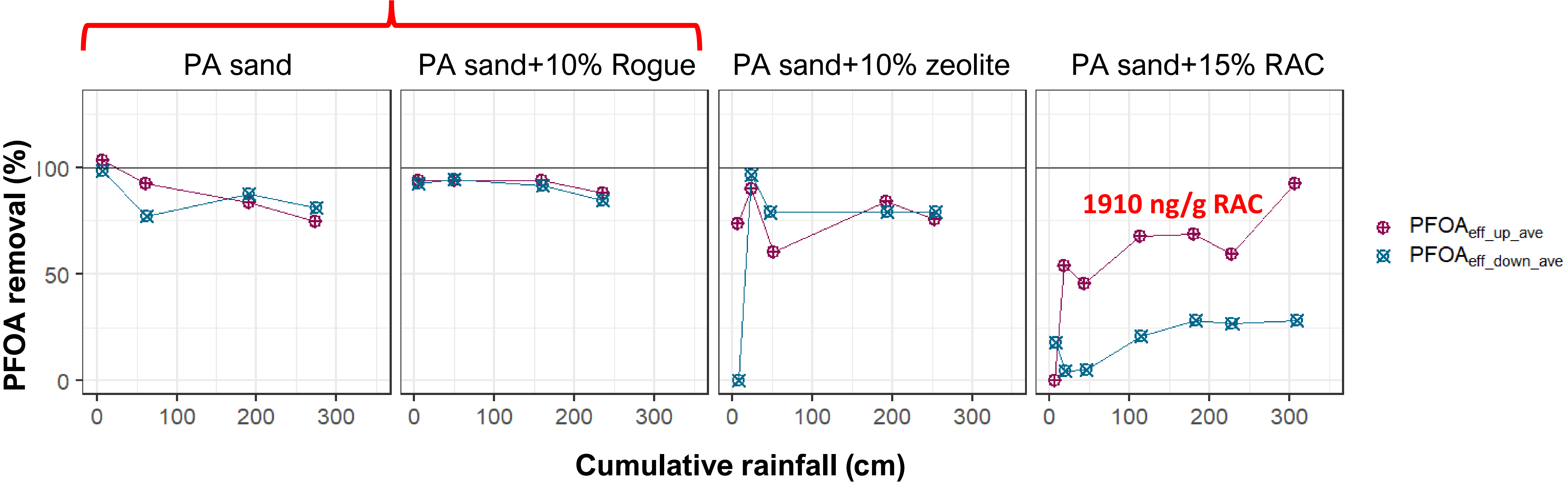
=

	Volumetric K_d (L/L)
PA	428
Rogue	408

Practical Application:

- Design engineer can choose the “right” ratio from available materials.

How much PFAS were removed?



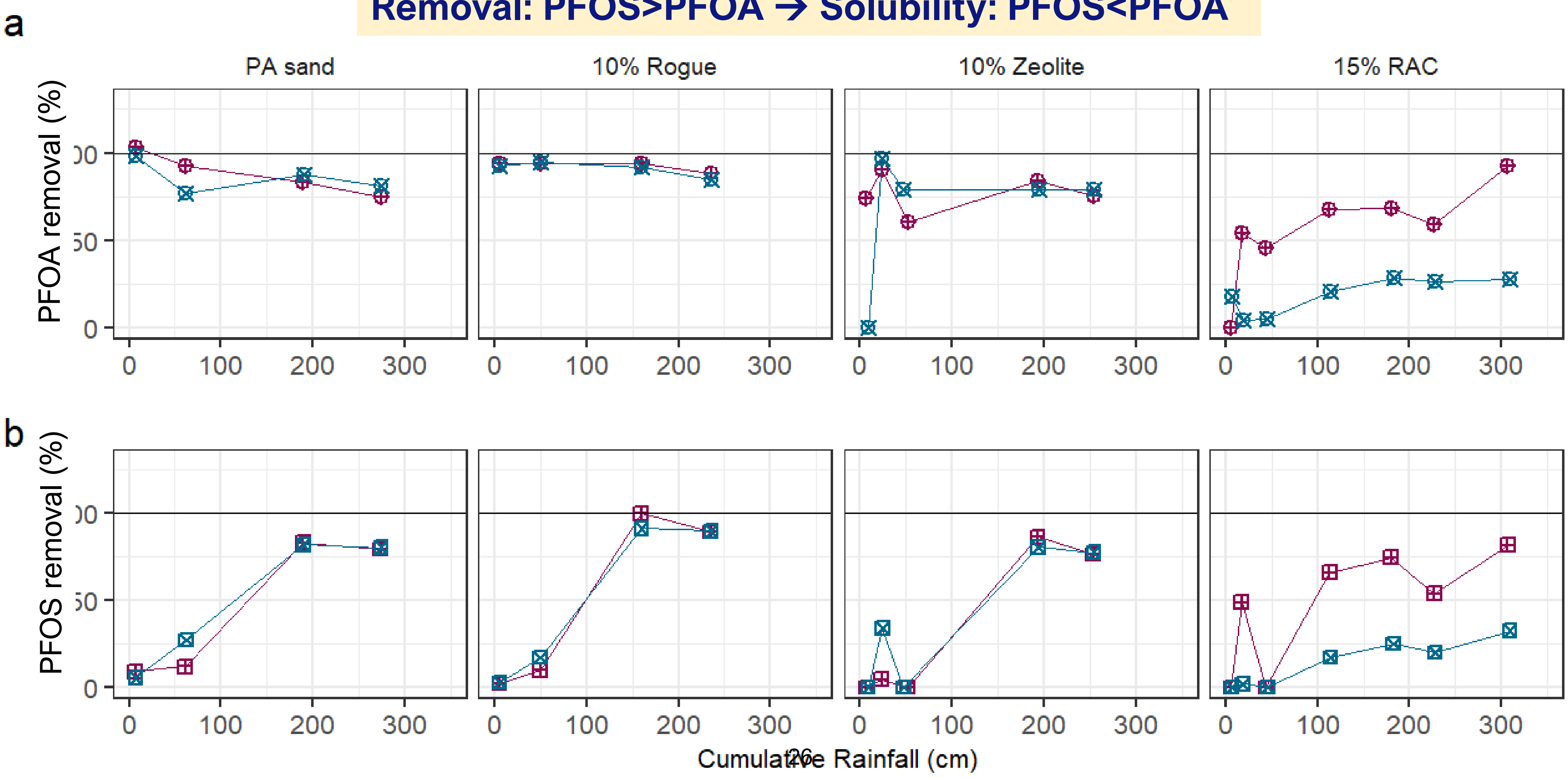
Ineffective

effective only initially

effective

PFOA vs. PFOS

Removal: PFOS>PFOA → Solubility: PFOS<PFOA



Which property is important for PFAS sorption?

Media	**$\mathrm{CEC_{Ba}}$**	**$\mathrm{CEC_X}$**	**Contact angle**	**$\mathrm{SSA_{BET}}$**
	(meq/100g)		(°)	(m^2/g)
PA sand	<2	2.1	54	0.02
Rogue biochar	15	25	55	547
Zeolite	7.6	28	63	15
RAC	3.6	5.5	72	841

Take-aways on media property

Outcomes	Practical applications
Cation exchange capacity (CEC_X) can be used to estimate the sorption affinity (K_d) of engineered media for dissolved Cu.	**CECx can be tested in advance to select the best material.**
Volumetric sorption affinity (ρK_d) needs to be considered when estimating media capacity in biofiltration systems.	**Design engineer can choose the "right" ratio from available materials.**
PFOA and PFOS are likely removed by media through hydrophobic interactions and **contact angle** may be an important parameter.	**Contact angle needs to be further studied to better understand PFAS sorption in biofiltration media.**

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Thank you!

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