

Designing Smarter Stormwater Systems at Multiple Scales with Transit Time
Distribution Theory and Real-Time Control

Emily Ann Parker

Dissertation submitted to the faculty of the Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
In
Civil Engineering

Stanley B. Grant, Chair
John C. Little
Megan A. Rippy
Todd Schenk

April 30, 2021
Manassas, VA

Keywords: urban runoff, green stormwater infrastructure, natural treatment, water supply,
low impact development, pollutant fate and transport, stormwater real-time control

Designing Smarter Stormwater Systems at Multiple Scales with Transit Time Distribution Theory and Real-Time Control

Emily Ann Parker

ABSTRACT

Urban stormwater runoff is both an environmental threat and a valuable water resource. This dissertation explores the use of two stormwater management strategies, namely green stormwater infrastructure and stormwater real-time control (RTC), for capturing and treating urban stormwater runoff. Chapter 2 focuses on clean bed filtration theory and its application to fecal indicator bacteria removal in experimental laboratory-scale biofilters. This analysis is a significant step forward in our understanding of how physicochemical theories can be melded with hydrology, engineering design, and ecology to improve the water quality benefits of green infrastructure. Chapter 3 focuses on the novel application of unsteady transit time distribution (TTD) theory to solute transport in a field-scale biofilter. TTD theory closely reproduces experimental bromide breakthrough concentrations, provided that lateral exchange with the surrounding soil is accounted for. TTD theory also provides insight into how changing distributions of water age in biofilter storage and outflow affect key stormwater management endpoints, such as biofilter pollutant treatment credit. Chapter 4 focuses on stormwater RTC and its potential for improving runoff capture and water supply in areas with Mediterranean climates. We find that the addition of RTC increases the percent of runoff captured, but does not increase the percent of water demand satisfied. Our results suggest that stormwater RTC systems need to be implemented in conjunction with context-specific solutions (such as spreading basins for groundwater recharge) to reliably augment urban water supply in areas with uneven

precipitation. Through a combination of modeling and experimental studies at a range of scales, this dissertation lays the foundation for future integration of TTD theory with RTC to improve regional stormwater management.

Designing Smarter Stormwater Systems at Multiple Scales with Transit Time Distribution Theory and Real-Time Control

Emily Ann Parker

GENERAL AUDIENCE ABSTRACT

Urban stormwater runoff contains a variety of pollutants. Conventional storm drain systems are designed to move stormwater as quickly as possible away from cities, delivering polluted runoff to local streams, rivers, and the coastal ocean – and discarding a valuable freshwater resource. By contrast, green stormwater infrastructure captures and retains stormwater as close as possible to where the rain falls. Green stormwater infrastructure can also help remove pollutants from stormwater through physical, chemical, and biological treatment processes. This dissertation describes two modeling approaches for understanding and predicting pollutant removal processes in green stormwater infrastructure (Chapters 2 and 3). Chapter 4 explores the implementation of smart stormwater systems, which use automated controllers and sensors to adaptively address stormwater management challenges. Through a combination of modeling and experimental studies at a range of scales, this dissertation lays the foundation for future improvements to regional stormwater management.

ACKNOWLEDGMENTS

I would like to thank my advisor, Stanley Grant, for his continual guidance and support, and most importantly, for always believing in me. Thank you to Meg Rippy for always being available to help with fieldwork and answer questions about plants, statistics, and everything else. Thank you to John Little and Todd Schenk for valuable discussions and feedback that informed this dissertation.

Thank you to my parents and my brother for all the emotional support along the way.

I'm incredibly grateful for all the friends and colleagues I gained over the course of my Ph.D. These valuable relationships make all the hard work worthwhile.

I would like to thank all my co-authors who contributed their time, energy, and brilliant insight to my manuscripts. I would also like to thank the many, many individuals who provided additional feedback and suggestions, and helped me with sampling, lab work, logistical support, and everything else behind the scenes.

I would like to acknowledge several funding sources that made my research possible: the U.S. National Science Foundation Partnerships for International Research and Education (OISE-1243543), the U.S. National Science Foundation Growing Convergence Research Program (Award 2021015), and the University of California Office of the President Multicampus Research Programs and Initiatives (MRP-17-455083). I would also like to gratefully acknowledge support from a Via Ph.D. Fellowship from the Virginia Tech Charles E. Via, Jr. Department of Civil and Environmental Engineering, a Samueli Endowed Fellowship from the University of California, Irvine Samueli School of Engineering, and a University of California, Irvine Provost Ph.D. Fellowship.

ATTRIBUTION

Several colleagues aided in the writing and research presented in this dissertation. A brief description of their contributions is included here.

CHAPTER 2: Predictive Power of Clean-Bed Filtration Theory for Fecal Indicator Bacteria Removal in Stormwater Biofilters

M. A. Rippy, A. S. Mehring, B. K. Winfrey, R. F. Ambrose, L. A. Levin, and S. B. Grant served as co-authors on this paper and assisted with experimental research, analysis, and editing.

CHAPTER 3: Predicting Solute Transport Through Green Stormwater Infrastructure with Unsteady Transit Time Distribution Theory

S. B. Grant, Y. Cao, M. A. Rippy, K. J. McGuire, P. A. Holden, M. Feraud, S. Avasarala, H. Liu, W. C. Hung, M. Rugh, J. Jay, J. Peng, S. Shao, and D. Li served as co-authors on this paper and assisted with experimental research, analysis, and editing.

CHAPTER 4: Can Smart Stormwater Systems Outsmart the Weather? The Limits of Stormwater Real-Time Control for Delivering Human and Environmental Benefits in Southern California

A. Sahin and J. A. Vrugt developed the campus runoff model used in this chapter.

TABLE OF CONTENTS

CHAPTER 1 Introduction	page 1
CHAPTER 2 Predictive Power of Clean Bed Filtration Theory for Fecal Indicator Bacteria Removal in Stormwater Biofilters	page 6
CHAPTER 3 Predicting Solute Transport Through Green Stormwater Infrastructure With Unsteady Transit Time Distribution Theory	page 30
CHAPTER 4 Can Smart Stormwater Systems Outsmart the Weather? The Limits of Stormwater Real-Time Control for Delivering Human and Environmental Benefits in Southern California	page 71
CHAPTER 5 Conclusion	page 91
REFERENCES	page 94
APPENDIX A Supporting Information for Chapter 2	page 119
APPENDIX B Supporting Information for Chapter 3	page 125
APPENDIX C Supporting Information for Chapter 4	page 145

Chapter 1

Introduction

Urban stormwater management has been a challenge for as long as urban areas have existed, but the nature of the problem has changed over time as cities and societies evolve. Urbanization fundamentally alters the hydrological response of an area to storms, by reducing local evapotranspiration and infiltration and increasing the volume of stormwater runoff generated by the urban landscape (Walsh et al., 2012). These hydrological alterations were initially treated as a strictly human flood risk problem. Accordingly, stormwater drainage systems, also known as municipal separate storm sewer systems (MS4s), were built to drain stormwater from the urban landscape to streams, lakes, and the coastal ocean with the goal of minimizing property damage and threat to public safety posed by floods. While MS4s generally accomplish their primary objectives of protecting property and lives (with notable exceptions during extreme precipitation events (e.g., Romero-Lankao & Norton, 2018)), by discharging untreated runoff to sensitive receiving waters they cause significant harm to the environment. Scientists have documented the negative environmental impacts of MS4s, and urban runoff is now largely recognized as a grand environmental challenge. For example, MS4s are a leading cause of surface water impairments in the US (National Academies, 2009; EPA, 1983; Ahn et al., 2005; Grebel et al., 2013; Reeves et al., 2004), and a primary driver of the urban stream syndrome (Walsh et al., 2005; Askarizadeh et al., 2015). The costs of these environmental impacts are staggering, as measured in human and ecosystem health (Given et al., 2006; Gaffield

et al., 2003; Walsh et al., 2005) and pollution cleanup and abatement (Shortle et al., 2001).

However, the nature of the problem is shifting once again. Communities facing drought and water scarcity are starting to recognize that MS4s discard a precious resource. In areas such as southern California, stormwater is now viewed as an important freshwater resource for satisfying non-potable water demand (Cousins et al., 2018; Gleick et al., 2018).

Urban runoff can be transformed into a valuable water resource through the adoption of green infrastructure, also known as low impact development (LID). LID technologies capture and treat urban runoff before it reaches sensitive receiving waters (Fletcher et al., 2008; Grant et al., 2013; Askarizadeh et al., 2015). The treated water can be used to support local groundwater supplies (if infiltrated) and as a source of non-potable water for irrigation and toilet flushing (if harvested) (Askarizadeh et al., 2015; Walsh et al., 2012; Grant et al., 2012; Jiang et al., 2015; Lim et al., 2013; Lim et al., 2015).

Biofilters (also known as rain gardens) are a particularly versatile form of LID technology. They are vertically oriented filtration systems in which runoff ponds at the top and percolates by gravity through planted and variably saturated filter media (Payne et al., 2015; Clar et al., 2004). Because they have relatively small areal footprints (e.g., compared to constructed wetlands) biofilters can be integrated into the urban landscape over a range of scales (Wong, 2006). They can also be engineered to achieve pre-specified levels of runoff harvesting and infiltration, for example with the goal of maintaining and/or restoring pre-urban flow regimes in streams (Askarizadeh et al., 2015; Burns et al., 2012).

However, engineers still lack robust modeling frameworks for predicting biofilter performance. In particular, many biofilter models do not account for the effects of transient unsaturated flow on pollutant removal. Many biofilter challenge experiments (in which a

pollutant of known concentration is applied to the inlet of a packed column of biofilter media) are conducted under steady-state flow conditions (e.g., Afrooz and Boehm, 2017; Zhang et al., 2011). While the results of these experiments are relatively straightforward to analyze (e.g., by converting them to an effective first-order decay constant), steady-state conditions are not representative of the highly transient storm flows experienced by biofilters in practice. Transit time distribution (TTD) theory, originally developed for hill-slope catchments, is a promising approach for addressing this limitation (Hrachowitz et al., 2016). TTD theory is a probabilistic, rather than physically-based approach, relying on a probability density function to describe the diversity of flow paths water (and contaminants) take as they pass through a catchment (or biofilter), i.e., the TTD of the system. TTDs are often assumed to be time-invariant (Kirchner et al., 2001; Barnes and Bonell, 1996; Ali et al., 2014; Hrachowitz et al., 2016). However, in practice, TTDs are highly variable in most hydrological systems (Hrachowitz et al., 2016; Kim et al., 2016; Ali et al., 2014), and this is especially the case in LID, in general, and biofilters, in particular, given the highly flashy nature of urban runoff (Walsh et al., 2005).

In addition to LID systems, an emerging approach to urban stormwater management is real-time control (RTC), or ‘smart’ stormwater systems. Arising from the development of the Internet of Things and research on smart city infrastructure, stormwater RTC holds promise for addressing the multiple interconnected challenges of urban stormwater and the need for dynamic and adaptable solutions in the face of climate change and urbanization (Kerkez et al., 2016; Yazdanfar and Sharma, 2015). Smart stormwater systems rely on an integrated network of sensors and control structures that allows for RTC of stormwater infrastructure at a systems level (Bartos et al., 2018) (see Figure 1), such as smart stormwater detention ponds that respond to weather forecasts by releasing stored water in advance of precipitation events (Carpenter et al.,

2014; Gaborit et al., 2013; Gaborit et al., 2016). These systems can ameliorate many of the problems faced by urban stormwater managers, including detecting and reducing combined sewer overflows (EPA 2018; Hofer et al., 2018; Lund et al., 2018; Campisano et al., 2016) and forecasting and reducing urban flood risk (Eggiman et al., 2017; Jacopin et al., 2001; Garofalo et al., 2017). While the smart stormwater technology itself has been investigated for a variety of stormwater benefits, the fundamental question of how best to deploy and scale the technology from a holistic and integrated standpoint remains unanswered (Mullapudi et al., 2017). In other words, stormwater systems designed to be smart technologically must be equally smart contextually – taking into account their hydrological, ecological, societal, and political setting.

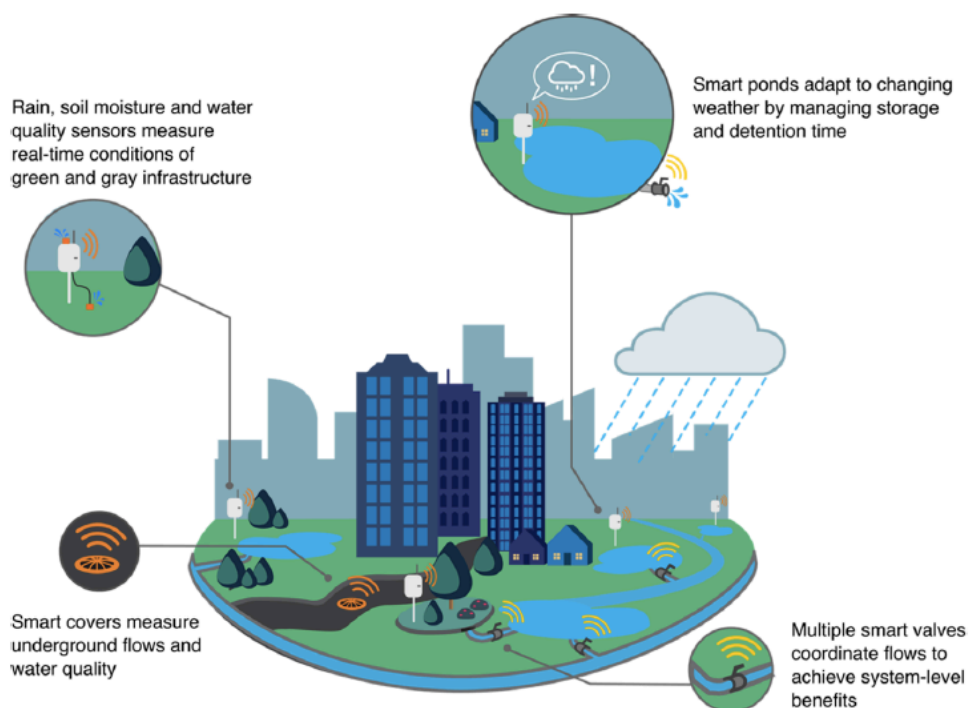


Figure 1. Example of an integrated real-time control network for urban stormwater management. Reprinted with permission from Kerkez, B.; Gruden, C.; Lewis, M.; Montestruque, L.; Quigley, M.; Wong, B.; Bedig, A.; Kertesz, R.; Braun, T.; Cadwalader, O.; Poresky, A.; Pak, C. Smarter Stormwater Systems. *Environ. Sci. Technol.* **2016**, 50 (14), 7267-7273. Copyright 2016 American Chemical Society.

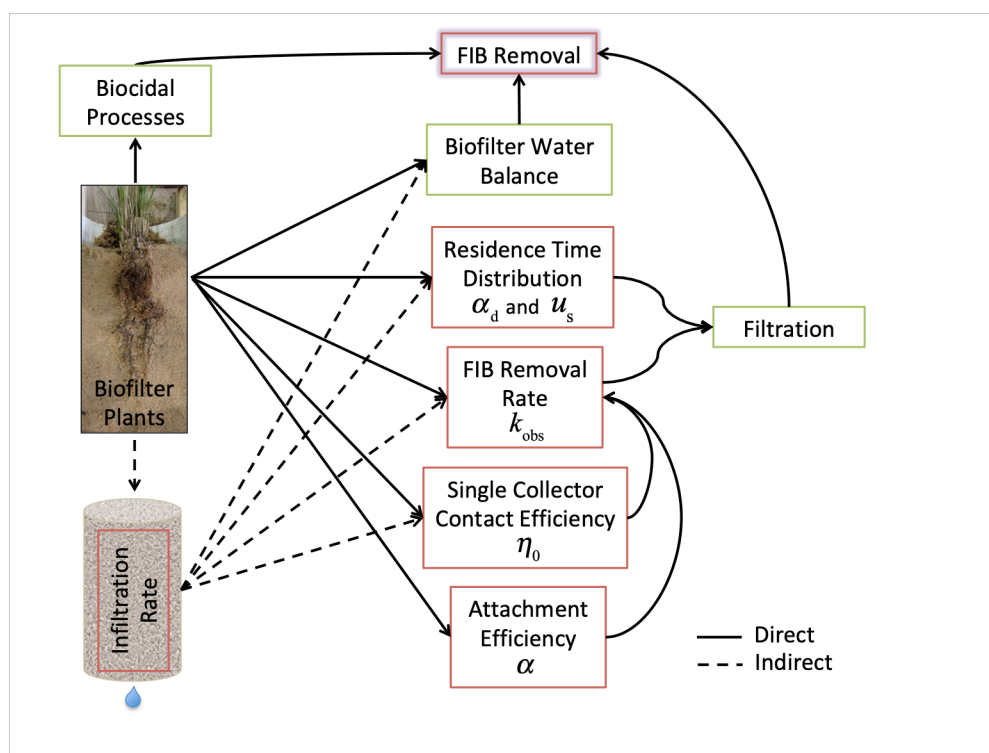
In this dissertation, I investigate stormwater capture and treatment systems at multiple scales, ranging from laboratory scale (Chapter 2), to field scale (Chapter 3), to university campus scale (Chapter 4). I first describe a study evaluating fecal indicator bacteria removal in laboratory-scale biofilters under steady state flow conditions (Chapter 2). The results of this study, anchored in steady state TTD theory and clean bed filtration theory, are a significant step toward understanding how physicochemical theories can be combined with hydrology, engineering design, and ecology to improve the water quality benefits of green infrastructure. Second, I describe unsteady TTD theory for modeling solute transport in biofilters, and its application to the results of a field-scale biofilter study conducted in Orange County, California (Chapter 3). I find that unsteady TTD theory can closely reproduce measured bromide breakthrough concentrations, provided that lateral exchange with the surrounding soil is accounted for. Third, I assess the implementation of stormwater RTC for areas with Mediterranean climates, using the University of California, Irvine campus as a test bed (Chapter 4). The results of this study indicate that Southern California's unevenly distributed precipitation limits the benefits of RTC stormwater capture systems. Finally, I offer conclusions and suggestions for future research to build on the work presented here.

Chapter 2

Predictive Power of Clean Bed Filtration Theory for Fecal Indicator Bacteria Removal in Stormwater Biofilters

This chapter reprinted with permission from:

Parker, E. A., Rippy, M. A., Mehring, A. S., Winfrey, B. K., Ambrose, R. F., Levin, L. A., & Grant, S. B. (2017). Predictive Power of Clean Bed Filtration Theory for Fecal Indicator Bacteria Removal in Stormwater Biofilters. *Environmental Science & Technology*, 51(10), 5703-5712. Copyright 2017 American Chemical Society.



Graphical abstract illustrating how biofilter plants may directly or indirectly (through changing infiltration rate) affect fecal indicator bacteria removal.

1. Introduction

Urban runoff poses both challenges and opportunities. Hydrological alterations associated with urbanization universally increase the volume of runoff and pollutant loads delivered to streams, lakes, and the coastal ocean during storms.¹⁻⁴ On the other hand, urban runoff can be transformed

into a valuable water resource through the adoption of green infrastructure, also known as low impact development (LID). LID technologies capture and treat urban runoff before it reaches sensitive receiving waters.⁵⁻⁷ The treated water can be used to support local groundwater supplies (if infiltrated) and as a source of non-potable water for irrigation and toilet flushing (if harvested).⁷⁻¹¹

Biofilters (also known as rain gardens or bioretention systems) are a particularly versatile LID technology. They are vertically oriented filtration systems in which runoff ponds at the top and percolates by gravity through planted and variably saturated filter media.^{12,13} Because they have relatively small areal footprints (e.g., compared to constructed wetlands), biofilters can be integrated into the urban landscape over a range of scales.¹⁴ They can also be engineered to achieve pre-specified levels of runoff harvesting and infiltration, for example with the goal of maintaining and/or restoring pre-urban flow regimes in streams.^{7,15}

Among their water quality benefits, biofilters may be useful for removing fecal indicator bacteria (FIB) from dry and wet weather urban runoff.¹⁶⁻²² FIB, which include *Escherichia coli* and enterococci bacteria, are routinely used by public health officials to assess the human health risk of recreating in fresh and marine surface waters.^{23,24} FIB are often present at high concentrations in urban runoff,²⁵⁻²⁸ and consequently thousands of runoff-impacted inland and coastal beaches in the U.S. are periodically closed to the public because FIB concentrations exceed state or federal limits.²⁹ The cost of these water quality impairments—measured in recreational waterborne illness,³⁰ lost recreational opportunity,³¹ and cleanup³²—is staggering. For example, deployment of LID and education programs to reduce stormwater runoff-associated FIB

pollution at recreational beaches in San Diego (California) could cost the city up to \$3.7 billion (2011 US dollars).³² For all of these reasons, there is an urgent need to understand how engineering design influences FIB removal in green infrastructure, in general, and biofilters, in particular.^{33,34}

Clean bed filtration theory (CBFT) may be helpful in this regard, as it is routinely used to design packed bed filtration systems for the removal of colloidal particles in water.^{35,36} CBFT predicts particle removal by physicochemical filtration, which involves two steps: (1) transport of particles to the surface of grains within a packed bed filter (described by a dimensionless “single collector contact efficiency”), and (2) attachment of particles to the grain surface (described by a dimensionless “attachment efficiency”). While physicochemical filtration is often cited as an important mechanism for FIB removal in biofilters,^{19,34,37-40} the theory’s many underlying assumptions may limit its utility for predicting the filtration of microorganisms in biofilters.^{37,41,42}

In this study we hypothesize that CBFT is a useful predictor of FIB removal in biofilters, but only when considered in the context of the many other factors that can affect treatment performance, such as the presence and type of upright vegetation in these systems, presence of a submerged zone, antecedent dry period (ADP), and biofilter age. To test this hypothesis we: (1) estimate observed first-order removal rates from new and previously published FIB challenge experiments that collectively capture a wide range of infiltration rates, degrees of saturation, ADPs, plant types, and study designs; (2) use CBFT to predict theoretical first-order removal rates for these experiments, ignoring the non-ideal conditions that might preclude a direct

application of the theory; and (3) use multiple linear regression to determine the fraction of the observed variance in FIB removal rates that can be attributed to CBFT versus other potentially important hydrological, engineering design, and ecological features.

2. Methods

Chandrasena et al. (2014) Experiment. Chandrasena et al.¹⁶ (hereafter referred to as “CH”) conducted a series of FIB removal experiments in laboratory biofilter columns (0.6 m deep, 0.15 m diameter). These were constructed with a layer of loamy sand at the top (0.3 m thick), a transition layer of washed coarse sand with 5% (v/v) finely shredded sugar cane mulch and 5% (v/v) pinewood chips without bark (0.2 m thick), and a gravel drainage layer at the bottom (0.1 m thick). This configuration is typical of biofilters in Australia: the transition layer is included to prevent the filter media from washing into the gravel layer, while the gravel layer is included to convey the treated water to drain pipes if the biofilter is lined, or shallow groundwater if the biofilter is unlined.¹² These previously published FIB challenge experiments were conducted by administering a single dose (either 3.7 L or 4.2 L, representing the different climatic conditions in the Australian cities of Melbourne and Perth, respectively) of synthetic stormwater, spiked with a pure culture of *E. coli* (ATCC #11775), to partially saturated biofilters. The synthetic stormwater consisted of dechlorinated tap water, sediment (passed through a 300- μ m sieve) from a nearby stormwater wetland, and reagent grade salts and heavy metals in final concentrations consistent with the chemical make-up of urban stormwater runoff in Melbourne.⁴³ *E. coli* concentrations (in units of most probable number (MPN) per 100 mL of sample) were quantified using the culture-based defined substrate technology IDEXX Colilert[®], implemented in a 96-well Quanti-Tray[®] format (IDEXX, Westbrook, ME). The biofilter columns (n=90) were placed in a

purpose-built greenhouse facility on the Monash University campus in Melbourne that allowed for realistic (i.e., outdoor) light and temperature variability, but prevented rain from falling on the columns, allowing the authors to control the volumes and quality of water entering the columns. Of the 90 columns, 20 were not planted (i.e., unplanted controls) while the other 70 were planted with a single species of upright vegetation. The palette of vegetation species included common biofilter plants spanning three different plant growth forms: two shrubs, one forb, and four graminoid species (consisting of one sedge, two grasses, and one lawn grass). The FIB challenge experiments consisted of seven dosing events conducted over the course of eight months, and therefore the age of the biofilters varied from approximately 8 to 16 months. Prior to the FIB challenge experiments, all columns (both vegetated and unplanted controls) were periodically watered with synthetic stormwater (defined above) with an ADP varying from 0 to 14 days, a typical range for the Melbourne area.⁴⁴ Here we focus on a subset of CH's FIB challenge experiments ($n = 196$) for which the reported infiltration rate was greater than $7.0 \times 10^{-6} \text{ m s}^{-1}$; this threshold represents the lower bound of infiltration rates for which our CBFT correlations apply (see later), and is at the low end of recommended hydraulic conductivities for biofilters in temperate and tropical environments.⁴⁵

2015/2016 Follow-Up Experiment. CH's challenge experiments were designed to evaluate FIB removal under a realistic range of field operating conditions. As a result, application of CBFT to these data is complicated by the fact that the columns were partially saturated and subject to transient flow during dosing events. We therefore carried out additional FIB challenge experiments to evaluate CBFT under more idealized (but less realistic) operating conditions. Six laboratory columns (0.8 m deep, 0.24 m diameter) were constructed in the Hydraulics Laboratory

at Monash University (Melbourne, Australia), using the same filter media as CH, arranged in slightly thicker layers: loamy sand (0.4 m), overlying a transition layer (0.3 m), overlying gravel (0.1 m). Three of the biofilters were planted with the sedge (graminoid) *Carex appressa* and three were unplanted (unplanted controls). The columns were illuminated with grow lights (12 hours on, 12 hours off) and watered twice per week with the same synthetic stormwater described earlier. Two sets of FIB dosing experiments were conducted, one when the biofilters were approximately 1 month old (July 2015) and another when they were approximately 9 months old (March 2016). While our biofilters were constructed based on the design described in CH, our FIB challenge experiments differed in six significant aspects: (1) source of FIB (a pure culture of *E. coli* spiked into synthetic stormwater in CH, secondary treated sewage from the Melbourne Eastern Treatment Plant in our experiments); (2) degree of saturation (biofilters were partially saturated in CH, biofilters were fully saturated in our experiment); (3) flow conditions (the pulse of FIB was applied to the biofilter as a single dose of spiked stormwater in CH, tap water was continuously flowing through our biofilters when the pulse of secondary-treated sewage was applied in our experiment, see SI Section 1 for details); (4) method used to assess FIB removal (measurements of the FIB concentration in a single composite sample of the biofilter effluent collected over approximately 24 h in CH, time-resolved measurements of FIB breakthrough curves in our experiment); (5) the FIB groups measured (*E. coli* in CH, *E. coli* and enterococci bacteria in our experiment); and (6) the range of infiltration rates interrogated ($I = 8 \times 10^{-6}$ to $7 \times 10^{-5} \text{ m s}^{-1}$ in CH, $I = 1 \times 10^{-4}$ to $2 \times 10^{-4} \text{ m s}^{-1}$ in our experiment). FIB concentrations (in units of MPN per 100 mL of sample) were quantified using IDEXX Colilert[®] (*E. coli*) and Enterolert[®] (enterococci bacteria) implemented in a 96-well Quanti-Tray[®] format (IDEXX, Westbrook, ME). Secondary-treated sewage is a reasonable (although imperfect) proxy

for urban runoff. The concentration of *E. coli* and enterococci bacteria in the secondary-treated sewage (about 2×10^4 to 2.5×10^4 MPN 100mL⁻¹ for *E. coli*, and about 3×10^3 to 7×10^3 MPN 100mL⁻¹ for enterococci bacteria) are within the range reported previously for stormwater runoff (110 to 2×10^6 MPN 100mL⁻¹ for *E. coli* (median 9×10^3 MPN 100mL⁻¹), and <1 to 8×10^5 MPN 100mL⁻¹ for enterococci bacteria (median 5×10^3 MPN 100mL⁻¹)).²⁶ However, the conductivity of the secondary-treated sewage (900 $\mu\text{S cm}^{-1}$) is high for stormwater runoff (event mean concentrations ranging from 211 to 730 $\mu\text{S cm}^{-1}$, maximum 1992 $\mu\text{S cm}^{-1}$).⁴⁶

Salt Pulse Experiment for Estimating Residence Time Distributions. In general, the treatment performance of packed bed filters depends on the rate at which contaminants are removed within the filter (e.g., by physicochemical filtration) and the residence time distribution of water passing through the filter.⁴⁷ To model the residence time distribution we adopted the dispersed plug flow model, which requires estimates for the interstitial velocity u_s (m s⁻¹) and dispersivity α_d (m); the former is a measure of how quickly water and mass are transported through the pore spaces of the filter by advection, while the latter represents longitudinal mixing within the filter by mechanical dispersion. The interstitial velocity can be represented as the ratio of the infiltration rate (or Darcy flux) (I , m s⁻¹) and the average porosity of the filter bed (θ , unitless): $u_s = I/\theta$. To estimate these parameters we carried out a salt pulse experiment on the same set of biofilter columns used in the 2015/2016 experiment (described above) under saturated and constant flow conditions. Two different conservative tracers were used, NaCl (in July 2015) and NaBr (in March 2016) (see SI Section 1 for details). Water samples (~80 per biofilter) were collected from the biofilter outlet at a variable sampling frequency (ranging from 0.067 to 1 min⁻¹) for approximately 4 hours following the addition of the salt pulse. The samples were then analyzed

for conductivity (NaCl, July 2015) and bromide concentration (NaBr, March 2016), using a handheld conductivity probe (model HQ40d, Hach, Loveland, CO) and an Orion bromide electrode (ThermoFisher Scientific, Waltham, MA); all measurements were calibrated using instrument calibration curves prepared immediately prior to the experiment. Values for α_d and u_s (and by inference θ) were then estimated by fitting the observed tracer breakthrough curves to the dispersed plug flow model:⁴⁷

$$C_{\text{exit}}^{\text{salt}}(\tau) = \frac{M_0^{\text{salt}}}{IA} \sqrt{\frac{u_s}{4\pi\tau\alpha_d}} \exp\left[-\frac{(L-u_s\tau)^2}{4\alpha_d u_s \tau}\right] \quad (1)$$

In this equation, $C_{\text{exit}}^{\text{salt}}(\tau)$ (g L^{-1}) represents the breakthrough concentration of salt at an elapsed time τ since the addition of the pulse, M_0^{salt} (g) represents the mass of salt added to the biofilter, L (m) is the biofilter depth, A (m^2) is the biofilter cross-sectional area, and all other variables have been previously defined. For the fitting step we adopted Bayesian inference using Monte Carlo Markov chain simulation with the DiffereNTial Evolution Adaptive Metropolis (DREAM) algorithm.^{48,49}

Observed Filtration Rate Constants (k_{obs}). CBFT represents particle removal in a filter by a first-order rate constant (k_{CBFT} , s^{-1} , calculated as described later). In this paper we compare the first-order removal rate constant predicted by CBFT, k_{CBFT} , with a first-order rate constant estimated from the FIB challenge experiment, referred to here as an “observed” first-order rate constant (k_{obs} , s^{-1}). Estimating the latter parameter involved two steps: (1) for each FIB challenge experiment (both ours and CH’s) we estimated the mass of FIB removed by passage through the biofilter (i.e., the mass ratio $M_{\text{exit}}^{\text{FIB}}/M_0^{\text{FIB}}$ where M_0^{FIB} and $M_{\text{exit}}^{\text{FIB}}$ represent the mass of

FIB, both in units of MPN, entering and exiting the biofilter column); and (2) for each mass ratio we calculated a corresponding first-order rate constant k_{obs} assuming that: (1) FIB undergo first-order removal; and (2) the residence time distribution can be described by the dispersed plug flow model (see last section). These two steps are detailed next.

The mass ratios were calculated as follows. CH assessed FIB removal by taking the ratio of the FIB concentration in a composite sample of the biofilter effluent (C_{exit}^{FIB} , MPN 100 mL⁻¹) and in the dose of spiked stormwater applied to the biofilter inlet (C_0^{FIB} , MPN 100 mL⁻¹): C_{exit}^{FIB}/C_0^{FIB} . Provided that roughly equal volumes of stormwater enter and exit the column, the mass ratio can be calculated directly from their reported concentration ratio: $M_{exit}^{FIB}/M_0^{FIB} \approx C_{exit}^{FIB}/C_0^{FIB}$. CH added 3.7 or 4.2 L of spiked stormwater to the column (depending on the climate being simulated), and reported that the volume of water drained from the biofilters declined with increasing ADP (average of 3.4 L after a three-day dry period versus 2.6 L after a two-week dry period); data on the water added and drained from each column were not reported. By equating the mass and concentration ratios, we may over- or under-estimate the actual FIB mass removal in CH's experiments (also note that water and FIB retained in one dosing event may be released in the next dosing event). For the 2015/2016 experiments, on the other hand, we calculated the initial FIB mass M_0^{FIB} from the product of the FIB concentration measured in the secondary-treated sewage and the volume of the sewage pulse added to the biofilter inlet. The mass of FIB exiting the biofilter M_{exit}^{FIB} was estimated by numerically integrating the measured FIB breakthrough curves, after subtracting out background FIB concentration (20 MPN 100 mL⁻¹ and 2 MPN 100 mL⁻¹ for *E. coli* and enterococci bacteria, respectively).

For each value of the mass ratio $M_{\text{exit}}^{\text{FIB}}/M_0^{\text{FIB}}$ estimated by the above approach, equation (2) (derivation in ref. 50) was numerically solved to yield a corresponding first-order rate constant k_{obs} given known values for the infiltration rate (I) and biofilter depth (L), in addition to porosity (θ) and dispersivity (α_d) values estimated from the salt pulse experiment (see last section). We used column-specific porosities and dispersivities (**Table S1, Supporting Information (SI), Appendix A**) for analyzing the 2015/2016 experiment; however, this information was not available for the CH biofilters so we adopted values averaged across the 2015/2016 experiment: $\theta = 0.4$ (both planted and unplanted biofilters), $\alpha_d = 0.04$ m (planted biofilters) and $\alpha_d = 0.01$ m (unplanted biofilters).

$$\frac{M_{\text{exit}}^{\text{FIB}}}{M_0^{\text{FIB}}} = \frac{4a \exp\left(\frac{L}{2\alpha_d}\right)}{(1+a)^2 \exp\left(a \frac{L}{2\alpha_d}\right) - (1-a)^2 \exp\left(-a \frac{L}{2\alpha_d}\right)} \quad (2)$$

$$a = \sqrt{1 + 4 \frac{k_{\text{obs}} \alpha_d \theta}{I}}$$

Observed Single Collector Contact Efficiency. One of the master variables in CBFT is the single collector contact efficiency η_0 (unitless), defined as the rate at which particles strike a collector over the rate at which particles flow toward the collector.³⁵ Equation (3), obtained from mass balance over a differential slice of a filter,³⁶ describes the relationship between the observed single collector contact efficiency η_{obs} (unitless) and the observed first-order rate constant k_{obs} . In this equation, d_c is the collector diameter (m), α (unitless) is the attachment efficiency (fraction of FIB-grain collisions that result in attachment), and all other variables are defined previously.

$$\eta_{\text{obs}} = \frac{2}{3} \frac{k_{\text{obs}} d_c \theta}{\alpha (1 - \theta) I} \quad (3)$$

Observed single collector contact efficiencies (η_{obs}) were calculated for each FIB challenge experiment by setting $\alpha = 1$ and substituting experimentally determined values for k_{obs} , I , θ (see above); the collector diameter ($d_c = 9.3 \times 10^{-4}$ m) was calculated from the median grain size of each filter media layer weighted by the corresponding thickness of each layer. The attachment efficiency was set to unity because, as noted in Tufenkji and Elimelech,⁵¹ theories for estimating this parameter are currently inaccurate. By setting $\alpha = 1$ in equation (3), our estimates for η_{obs} represent lower-limit values.

Theoretical Single Collector Contact Efficiency. Typically, three transport mechanisms are considered when predicting the theoretical single collector contact efficiency η_0 : (1) particle collision with the collector by interception (η_I , particles moving along a streamline intercept collectors due to physical size); (2) gravitational sedimentation (η_G , particles with densities greater than water settle onto the collector surface); and (3) Brownian diffusion (η_D , Brownian motion of particles resulting in contact with a collector):⁵¹

$$\eta_0 = \eta_D + \eta_I + \eta_G \quad (4)$$

Tufenkji and Elimelech⁵¹ developed a set of correlation equations for predicting η_D , η_I , and η_G in saturated porous media, based on numerical simulations of the convective-diffusion equation for particle transport around a collector, accounting for both hydrodynamic interactions and van der Waals forces that develop between particle and collector on close approach.⁵¹ We used these

correlations and equation (4) to calculate theoretical values of η_0 using parameter values appropriate for the biofilter experiments included in this study (see SI Section 2).

Multiple Linear Regression. To determine if CBFT is predictive of FIB removal in biofilters we estimated the fraction of variance in the observed removal rate (k_{obs}) that is explained by the CBFT-predicted removal rate (k_{CBFT} , calculated as described below) as compared to other environmental and biofilter design features, using multiple linear regression (MLR) conducted in R software.⁵² Two different MLR models were evaluated: (1) the Total Model which included data from both CH and the 2015/2016 experiments, and (2) the Partial Model which included data only from CH (2015/2016 experiments excluded). For the Partial Model we adopted the observed filtration rate (k_{obs}) as the dependent variable, and the following predictor variables: (1) k_{CBFT} (s^{-1}), (2) biofilter age (months), (3) ADP (days), (4) submerged zone presence or absence, and (5) a set of three binary dummy variables for plant type (e.g., shrub, graminoid, or forb). The same dependent and predictor variables were adopted for the Total Model, but a new binary predictor variable “Study” was added to account for possible effects of differences in the two studies. Theoretical filtration rate constants (k_{CBFT}) were calculated from equation (5) based on Tufenkji and Elimelech’s theoretical correlations for the single collector contact efficiencies (η_0 , see above and SI Section 2), known values of the infiltration rate (I) and collector diameter (d_c), and the average column porosities (θ) estimated from the salt pulse experiments:

$$k_{\text{CBFT}} = \frac{3(1-\theta)I}{2d_c\theta}\eta_0 \quad (5)$$

Equation (5) is obtained by rearranging equation (3), substituting k_{CBFT} for k_{obs} , and assuming the attachment efficiency is equal to unity. FIB die-off and re-growth were not included as

predictor variables because measurements of their respective rates were available for very few of the filtration experiments included in this study. Furthermore, these last two rates would not be useful predictor variables because they depend on features of urban runoff not typically measured in practice, including the concentrations of dissolved organic carbon and phosphorous, and the density and grazing rates of micro- and meso-faunal grazers (e.g., predacious protozoa).
37,53

Prior to performing the MLR, the variance inflation factor (VIF) was calculated for all predictor variables to identify instances of multicollinearity. No significant multicollinearity was detected ($VIF < 5$),⁵⁴ indicating that all variables were suitable for co-evaluation in the MLR analyses. Models were ranked using the Bayesian Information Criterion (BIC).⁵⁵ Candidate best-fit model sets (within 2 BIC units of the highest ranked model) were identified and further evaluated relative to predictive ability using leave-one-out cross validation with Root Mean Squared Error (RMSE) as the validation metric.⁵⁶ We then selected the best-fit Total Model and Partial Model as those with the lowest average RMSE (weighted average across all leave-one-out estimates) in their respective candidate sets. The coefficient of determination (R^2) was calculated for each best-fit model as an indicator of overall model fit. The relative importance of each predictor variable (i.e., the proportionate contribution made to R^2) was estimated using the averaging over ordering method proposed by Lindeman, Merenda and Gold.⁵⁷ Because the relative importance of a predictor can differ from its theoretical importance (i.e., the response magnitude for a given change in the predictor)⁵⁷ theoretical importance was assessed using estimated effects plots.

3. Results and Discussion

Single Collector Contact Efficiencies. The single collector contact efficiency (η_0) includes contributions from interception (η_i), diffusion (η_D), and gravitational sedimentation (η_G) (see equation (4) and discussion thereof). To the extent that Tufenkji and Elimelech's correlation⁵¹ applies to our dataset, their theory predicts that Brownian diffusion is the dominant transport mechanism by which FIB encounter biofilter media; i.e., $\eta_0 \approx \eta_D$ over most infiltration rates (compare solid bold and dashed curves in **Figure 1**).

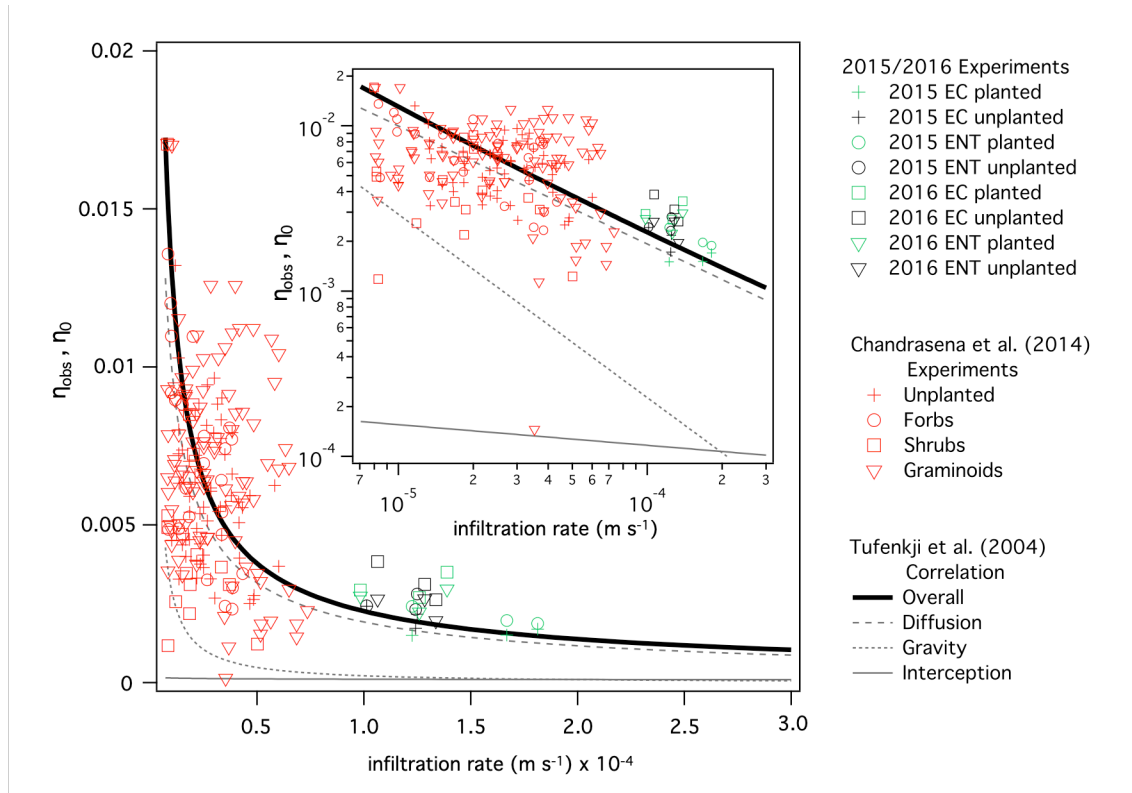


Figure 1. Observed single collector contact efficiencies estimated from the 2015/2016 experiment (black and green symbols) and CH's experiment (red symbols), compared to Tufenkji and Elimelech's theoretical correlations for single collector contact efficiency (black (overall) and gray (individual transport mechanisms) curves). **Inset:** The same comparison, displayed on a log-log plot.

The theoretical single collector contact efficiency declines sharply with increasing infiltration rate. This result can be understood by noting that, at higher infiltration rates, FIB are swept past

collectors more quickly (thus reducing the opportunity for FIB-grain collisions by one or more transport mechanisms) and hydrodynamic repulsive forces between FIB and grains become stronger on close approach (thus reducing the likelihood that FIB-grain collisions will actually occur). Single collector contact efficiencies calculated from the FIB challenge experiments (η_{obs}) follow a similar trend, although there is considerable scatter about the theoretical curve (compare data points with thick solid curve). Interestingly, some of this scatter is plant specific—for example, it appears that biofilters planted with shrubs are consistently biased low relative to Tufenkji and Elimelech’s correlation (compare red open squares and dark black curve in **Figure 1**).

First-Order Filtration Rates. CBFT is a poor predictor of the first-order FIB removal rate constants calculated from CH’s experiment (red symbols, **Figure 2A**). In particular, CH’s FIB removal rate constants exhibit nearly 100-fold more variability compared to the FIB removal rate constants predicted by CBFT. By contrast, the observed and CBFT-predicted first-order removal rates are in relatively close agreement for the 2015/2016 experiments (black and green symbols, **Figure 2A**). One interpretation of these results is that CBFT is a better predictor of observed removal rates when the experimental design of the FIB challenge experiments adheres more closely to the assumptions inherent in our analysis—in particular, several of the key assumptions of the dispersed plug flow model (steady flow and fully saturated conditions, see equation (2)) were more closely approximated in our 2015/2016 experiment than in CH’s experiment. On the other hand, the variability in CH’s k_{obs} may simply reflect the many treatments tested in their study on FIB removal, including five different plant types, two different ADPs, four different biofilter ages, and the presence/absence of submerged zones. Indeed, under realistic field

operating conditions it is likely that many different factors—perhaps including CBFT—will influence observed FIB removal rates.

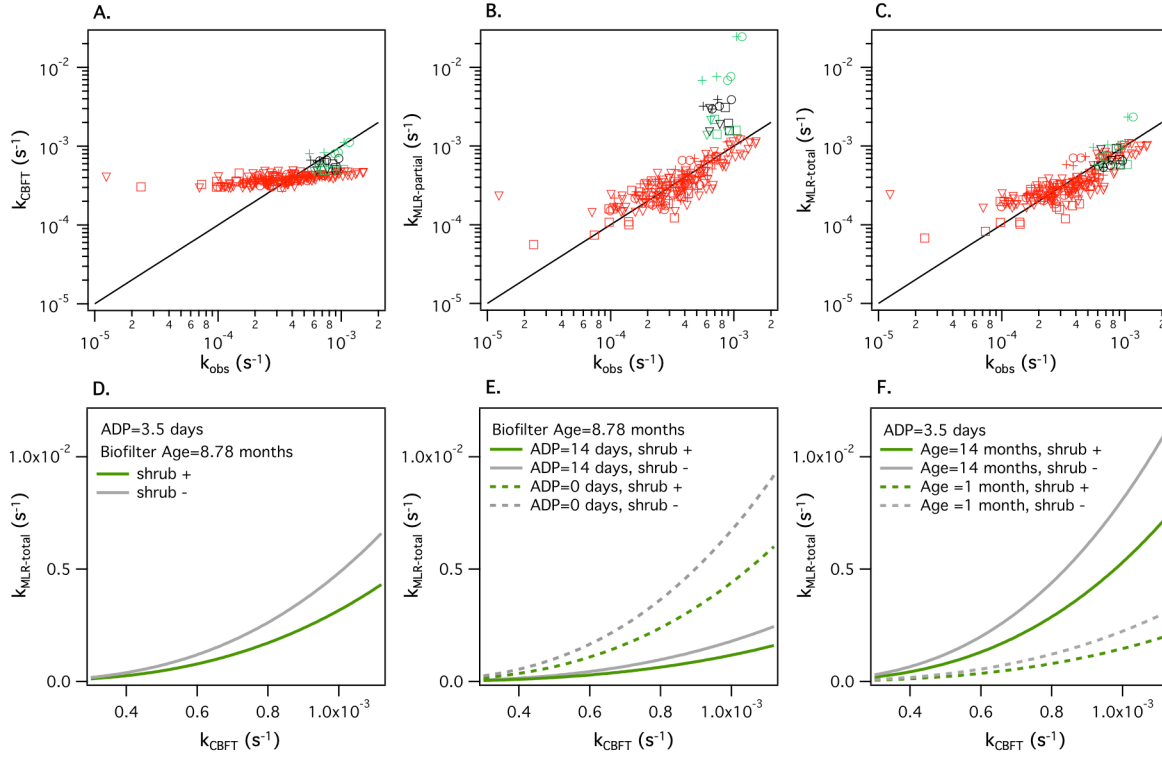


Figure 2. (A, B, C) Cross-plots of experimentally observed first-order FIB removal rate constants and (A) first-order rate constants predicted from CBFT, (B) first-order rate constants predicted from the Partial Model, and (C) first-order rate constants predicted from the Total Model. The black line in each plot is the 1:1 line; symbols are consistent with **Figure 1**. (D, E, F) Partial effect plots illustrating how the first-order removal rate constant predicted by the Total Model increases with the CBFT-predicted first-order removal rate constant, and how this response is influenced by shrubs (D, E, F), antecedent dry period (ADP) (E), and biofilter age (F).

Multiple Linear Regression. MLR modeling supports our hypothesis that CBFT can predict observed filtration rates, but only when considered in the context of other environmental, ecological, and biofilter design variables. The selected predictor variables were nearly identical for the Partial Model (CH’s data alone) and Total Model (CH’s and our 2015/2016 data) (**Table S2**). The Partial Model consists of four significant predictor variables (k_{CBFT} , ADP, column age, and shrub presence/absence) while the Total Model consists of the same four variables plus an

additional (fifth) variable “Study”, signaling the presence of a significant study-specific effect (see above discussion of across-study differences). The magnitude of the “Study” effect is evident in **Figures 2B,C**, where the 2015/2016 k_{MLR} values (black and green symbols) are clear outliers ($k_{\text{MLR}} \gg k_{\text{obs}}$) when predicted using the best-fit Partial Model (**Figure 2B**) but fall along the 1:1 line ($k_{\text{MLR}} \approx k_{\text{obs}}$) when “Study” is included in the Total Model (**Figure 2C**).

Both the Partial Model and Total Model explain a substantial fraction of the observed variance in the FIB removal rate constant k_{obs} (approximately 66%; see **Table S2**). Roughly half of the variance captured by the MLR models is attributable to the CBFT-predicted rate constant k_{CBFT} (31% Total Model; 35% Partial Model). The remaining variance, in order of decreasing importance, is attributable to: (1) ADP (14% Total Model; 18% Partial Model); (2) Study (8% Total Model; omitted in the Partial Model); (3) column age (7% Total Model; 8% Partial Model); and (4) shrub presence/absence (6% Total Model; 5% Partial Model, **Table S2**). These results imply that, while k_{CBFT} alone cannot be used to estimate k_{obs} (**Figure 2A**), the former is a strong predictor of the latter when considered together with other (individually subordinate but collectively strong) variables pertaining to hydrology, biofilter maturity, and biofilter ecology (**Figures 2B, 2C**). Interestingly, ADP, which appears as the second most important variable in both models (compare averaging over ordering (LMG) scores in **Table S2**), has been identified as a key factor affecting the removal of stormwater pollutants by biofilters in other studies.^{16,17,58-}

61

Partial Effect Plots. Partial effects plots (calculated from the Total Model) reveal how the influence of CBFT on observed FIB removal rates is modulated by ADP, biofilter age, and the

presence of shrubs (**Figure 2D-F**). Consistent with the results presented in **Table S2**, k_{MLR} increases monotonically with increasing k_{CBFT} . However, this relationship is weakened by the presence of shrubs (**Figure 2D**) and longer ADP (**Figure 2E**) and is enhanced in older biofilters (**Figure 2F**). Surprisingly, plants play a relatively minor role in both the Total Model and Partial Model, except to reduce FIB removal rates when the biofilters are planted with shrubs. On its face this result contradicts CH's finding that the choice of plant species strongly influences FIB removal.³⁹

However, the above contradiction is resolved by taking into account the distinction between a first-order removal rate for FIB (the focus of this study) and overall FIB removal (the focus of CH's study). We focused on the first-order removal rate because it is the more fundamental parameter; i.e., the overall removal rate achieved by a biofilter will depend on both the rate at which FIB are removed by one or more mechanisms (k_{obs}) and the advective and dispersive transport processes that determine the biofilter's residence time distribution.⁴⁷ Thus, plants can affect overall FIB removal in at least three potential ways: (1) creating new mechanisms by which FIB are removed in the biofilter, for example, by growing roots that serve as collectors for FIB,⁴⁰ creating habitat for micro- and meso-faunal grazers that remove FIB through predation,^{19,37,38,62} and altering the survival rates of FIB through, for example, competition for nutrients;³⁴ (2) altering the single collector contact efficiency and attachment efficiency through promotion of biofilm growth,⁶³ generation of surface-active plant exudates,⁶⁴ and creation of preferential flow paths that limit stormwater/biofilter media interactions;^{65,66} and (3) changing the infiltration rate which, in turn, alters the biofilter's residence time distribution,⁶⁶ the single-

collector contact efficiency (see **Figure 1**), and ultimately the first-order filtration rate (see equation (5)).

More generally, the above three categories of plant effects can be grouped into those where the plants directly influence FIB removal (categories (1) and (2)) versus those in which plants indirectly influence FIB removal by altering the infiltration rate (category (3)). With the exception of shrubs, our MLR analysis suggests that the type of plants (or even the presence of plants) does not affect the value of k_{obs} (see **Table S2** and discussion above). Therefore, for the experiments analyzed here, plant selection influences FIB removal indirectly by changing the infiltration rate, not directly by changing the mechanisms of FIB removal, or altering η_0 in ways not already accounted for by CBFT theory. This interpretation is consistent with CH's assessment that, relative to FIB removal, "highly performing plant species were associated with lower infiltration rates."²⁰

Our MLR results also suggest that, all else being equal, FIB removal rates increase with increasing biofilter age and decreasing ADP. The influence of increasing biofilter age on FIB removal rate may reflect an increase in the number of ways FIB can be removed by the biofilter as it ages, including "filter ripening" (where previously deposited particles serve as additional collectors in the absence of electrostatic inter-particle repulsion),⁶⁷ biofilm formation (and associated increases in the attachment efficiency),⁶³ and/or the progressive growth of micro- and meso-faunal grazers over time.^{19,37,38} The influence of ADP on FIB removal rate, on the other hand, may reflect the tendency of preferential flow paths (including fissures and macropores) to develop after long ADPs.^{34,39} While preferential flow paths are associated with increased

infiltration rates (already accounted for by CBFT and hence incorporated into the value of k_{CBFT} , see above),^{34,39} they also reduce the number of FIB/collector collisions that can occur as FIB quickly pass through the biofilter (an effect that is not accounted for by CBFT and thus not included in k_{CBFT}). Because ADP can fundamentally alter the mechanisms by which FIB are removed in the biofilter, it is not surprising that this quantity emerges as a secondary but significant predictor of k_{obs} in our MLR analysis.

Finally, it is worth noting that different removal mechanisms may operate over different timescales. For example, FIB may attach to media grains by physicochemical filtration over the timescale of a storm, and then undergo permanent removal by micro- or meso-faunal grazing over longer time scales.^{19,37}

Infiltration Rate and Catchment Ratio as Master Design Variables. The importance of infiltration rate becomes even more evident if one considers not only the biofilter, but also the drainage system within which the biofilter is embedded. As illustrated in **Figure 3** (see inset), during a storm event the fraction of runoff from the catchment (Q , L s^{-1}) that can be processed by the biofilter is limited by the biofilter's infiltration rate (I , m s^{-1}) and its surface area (A , m^2); i.e., when $Q < IA$ all runoff will pass through the biofilter, whereas when $Q > IA$ only a portion of runoff (equal to IA) will pass through the biofilter (the difference, $Q - IA$ will by-pass the biofilter and, for example, flow directly to the storm sewer system). Thus, at the catchment scale, a potential trade-off arises, in which higher infiltration rates increase the volume of runoff passing through the biofilter (all else being equal), but reduce the overall FIB removal achieved for the various reasons described above (e.g., reduction in the single collector contact efficiency

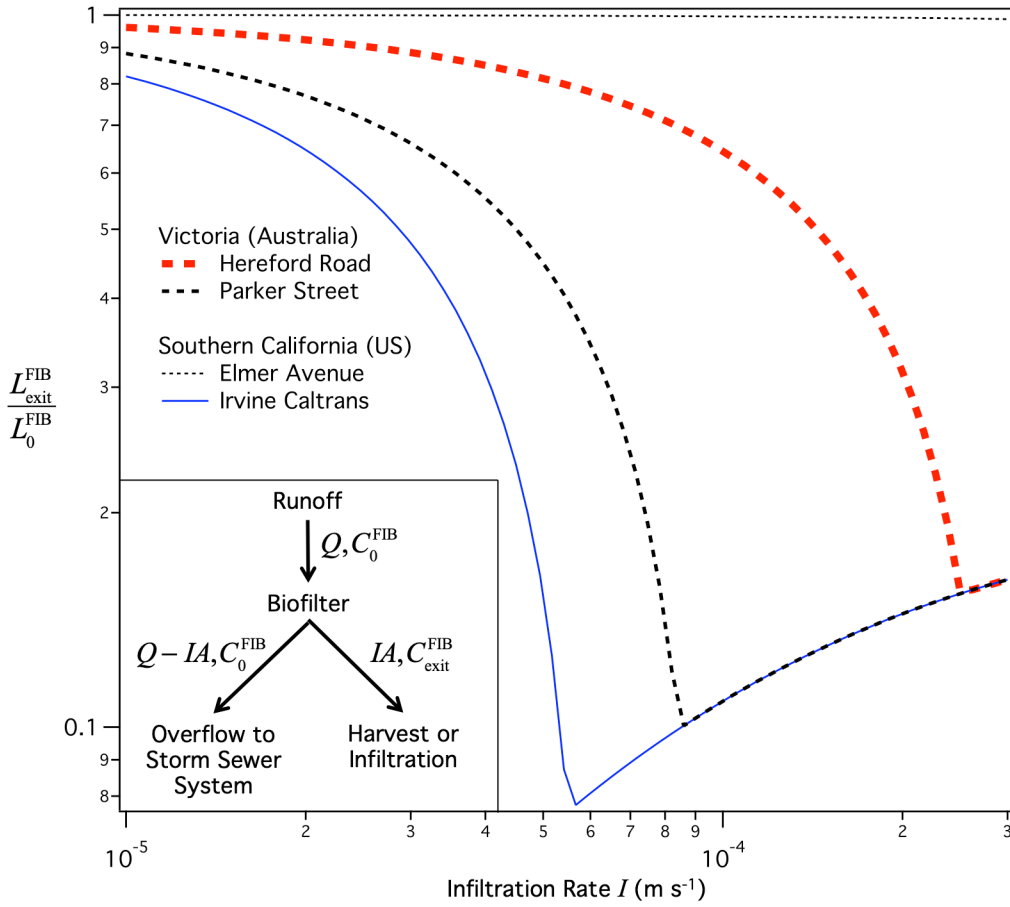


Figure 3. Design curves illustrating how the mass of FIB removed by a biofilter-catchment system depends on infiltration rate for four example sites in southern California and Victoria, Australia. Three of the biofilter sites (Irvine Caltrans, Hereford Road, and Parker Street) display an “optimal” infiltration rate, where $L_{\text{exit}}^{\text{FIB}}/L_0^{\text{FIB}}$ is minimized. **Inset:** Biofilter water balance, where C_0^{FIB} and $C_{\text{exit}}^{\text{FIB}}$ (MPN L^{-1}) are the concentrations of FIB entering and exiting the biofilter, respectively, Q (L s^{-1}) is the volumetric flow rate of stormwater runoff entering the biofilter, I (m s^{-1}) is the biofilter infiltration rate, and A (m^2) is the biofilter surface area. If $Q > IA$ only a fraction (IA) of the incoming runoff will be treated by the biofilter while the rest will bypass the biofilter and flow directly to the storm sewer system. Depending on biofilter design, the treated stormwater runoff is harvested, infiltrated, or released back to the storm sewer system.

and mean residence time in the biofilter). This trade-off can be ameliorated by adding features that store runoff over the course of a storm (e.g., by increasing the ponding depth of the biofilter, or creating off-line storage).

The above trade-off can be illustrated by the following simple analysis, in which we assume that minimal on-site storage exists or the storage is fully utilized. Under such conditions, the performance of the biofilter/catchment system can be approximated from a simple steady-state analysis of the fraction of FIB load (FIB s^{-1}) flowing out of the catchment (L_0^{FIB}) that is not removed by the biofilter ($L_{\text{exit}}^{\text{FIB}}$):

$$\frac{L_{\text{exit}}^{\text{FIB}}}{L_0^{\text{FIB}}} = \begin{cases} \frac{M_{\text{exit}}^{\text{FIB}}}{M_0^{\text{FIB}}}, & \text{if } \frac{IA}{Q} \geq 1 \\ \frac{IA}{Q} \left(\frac{M_{\text{exit}}^{\text{FIB}}}{M_0^{\text{FIB}}} - 1 \right) + 1, & \text{if } \frac{IA}{Q} < 1 \end{cases} \quad (6)$$

$$\frac{M_{\text{exit}}^{\text{FIB}}}{M_0^{\text{FIB}}} \leq 1$$

The ratio $M_{\text{exit}}^{\text{FIB}}/M_0^{\text{FIB}}$ represents the steady-state fraction of FIB mass not removed by the biofilter (see equation 2). We applied equation (6) to estimate $L_{\text{exit}}^{\text{FIB}}/L_0^{\text{FIB}}$ for four different biofilter-catchment systems in Southern California (Irvine Caltrans and Elmer Avenue) and Victoria, Australia (Hereford Road and Parker Street) assuming a rainfall intensity of $i = 10 \text{ mm hr}^{-1}$ in each case (**Figure 3**). For simplicity, we assume: (1) the biofilters all have the same basic design (i.e., same bed media and depth) but differ in biofilter area (A) and impervious catchment area (A_c) (**Table S3**); and (2) an impervious runoff coefficient of unity and thus all rain falling on the catchment will generate runoff ($Q = iA_c$). For each of these systems we evaluated equation (6) over a range of infiltration rates ($I = 10^{-5}$ to $3 \times 10^{-4} \text{ m s}^{-1}$). The ratio $M_{\text{exit}}^{\text{FIB}}/M_0^{\text{FIB}}$ in equation (6) was estimated from equation (2), after replacing k_{obs} with the Total Model

predictions of k_{MLR} and assuming the following biofilter conditions: (1) one year old; (2) one week ADP; (3) shrubs present; and (4) average porosity and dispersivity values obtained from the salt pulse experiment.

For three of the biofilter sites (Irvine Caltrans, Hereford Road, and Parker Street) there is a clear optimal infiltration rate at which FIB mass breakthrough L_{exit}^{FIB}/L_0^{FIB} is minimized (**Figure 3**). The FIB removal achieved at this optimal infiltration rate is strongly dependent on the catchment ratio, defined as the ratio of biofilter area to catchment area ($CR = A/A_c$, **Table S3**).⁴⁴ The system with the lowest CR (Elmer Avenue) exhibits near complete FIB breakthrough across the full range of infiltration rates evaluated. In this case, the biofilter receives too much runoff (from too large a catchment area) and as a result most of the storm water generated by the catchment bypasses the biofilter and flows directly to the storm drain (or, in the case of Elmer Avenue, other LID features including porous pavement, bioswales, or an underground infiltration gallery⁶⁸). As CR increases (Hereford < Parker < Caltrans) a larger fraction of the stormwater passes through the biofilter, the optimal infiltration rate shifts toward lower values, and more FIB removal is achieved at the optimal infiltration rate. One of the most pervasive problems with the long-term performance of biofilters is their tendency to accumulate fine particles and clog over time.⁶⁹ According to this simple analysis, a decline in infiltration rate (associated with clogging) may increase or decrease FIB removal depending on where a biofilter starts out on the design curves illustrated in **Figure 3**.

Our MLR model should be viewed as a prototype subject to future refinement, for example to account for the effects of field versus laboratory studies, different classes of microorganisms

(viruses, bacteria, protozoans), plant mono-cultures versus plant poly-cultures, and soil invertebrates. Practically speaking, the results presented here (together with their future refinements) could be easily incorporated into standard LID design software packages, such as the U.S. Environmental Protection Agency's Storm Water Management Model (SWMM).⁷⁰

Chapter 3

Predicting Solute Transport through Green Stormwater Infrastructure with Unsteady Transit Time Distribution Theory

This chapter reprinted with permission from:

Parker, E. A.; Grant, S. B.; Cao, Y.; Rippey, M. A.; McGuire, K. J.; Holden, P. A.; Feraud, M.; Avasarala, S.; Liu, H.; Hung, W. C.; Rugh, M.; Jay, J.; Peng, J.; Shao, S.; Li, D. (2021) Predicting Solute Transport Through Green Stormwater Infrastructure with Unsteady Transit Time Distribution Theory. *Water Resources Research*, 57 (2), e2020WR028579. Copyright 2020 the authors.

1. Introduction

Green stormwater infrastructure (GSI) provides many benefits beyond the retention and detention of urban stormwater flows (Walsh et al., 2005; Walsh et al., 2012), including improved water quality, urban heat mitigation, habitat creation in support of urban biodiversity, carbon sequestration, recreational opportunities, and mental health (BenDor et al., 2018; Engemann et al., 2019; Grant et al., 2012; Grant et al., 2013; Grebel et al., 2013; Keeler et al., 2019; National Academy of Sciences, 2016; Raymond et al., 2017; Walsh et al., 2016). In this paper we focus on the water quality benefits of an increasingly popular form of GSI called biofilters, also known as bioretention systems or rain gardens. As illustrated in Figure 1a, these vertically oriented systems filter water through planted soil or sand-based media and are easily integrated into the urban landscape over a range of scales (Grant et al., 2013; Roy-Poirier et al., 2010; Wong, 2006). Their possible features include: (1) a ponding zone that retains water prior to infiltration; (2) biological components including upright vegetation and naturally colonizing soil invertebrates and microorganisms; (3) engineered filter media (sand, sandy loam, or loamy sand with or without media amendments (e.g., biochar; Boehm et al., 2020; Mohanty & Boehm, 2014)); (4) a

coarse sand transition layer; (5) a drainage layer consisting of coarse sand or fine gravel which can be lined or unlined and with or without an underdrain; (6) an overflow structure that releases excess stormwater; and (7) a raised outlet to facilitate the formation of a permanently wet “submerged zone” (Clar et al., 2004; Davis et al, 2009; Kim et al., 2003; Payne et al., 2015; Rippy, 2015).

The water quality benefits attributable to GSI are often quantified based on the fraction of stormwater pollutants (measured on a concentration or mass basis) removed during laboratory or field challenge experiments (Bedan & Clausen, 2009; Davis et al., 2009; Feng et al., 2012; Hatt et al., 2009; Kranner et al. 2019; Li et al., 2012; Li & Davis, 2014; Parker et al., 2017; Ulrich et al., 2017). Much of this research has focused on the link between system design and pollutant removal, for example how the choice of plant species and the presence or absence of a submerged zone influences the removal of nutrients (e.g., Kim et al., 2003; Payne et al. 2018; Read et al., 2008; Read et al., 2009; Ryciewicz-Borecki et al., 2017) and how media amendments influence the removal of microbial contaminants and heavy metals (e.g., Li et al., 2016; Mohanty & Boehm, 2014; Zhang et al., 2010). The effects of transient unsaturated flow, a defining feature of biofilters and GSI generally, are less often considered. Occasionally, transient unsaturated flow is indirectly acknowledged through experimental designs that incorporate an antecedent dry period between stormwater dosing events (Chandrasena et al. 2014a; Payne et al. 2014). Similarly, biofilter design guidelines often recommend the inclusion of a submerged zone so that a portion of stormwater passing through the biofilter spends a longer time undergoing treatment (e.g., nitrogen removal by denitrification) between storms (LeFevre et al., 2015; Payne et al. 2015). Yet, a detailed understanding of how transient unsaturated flow influences contaminant removal remains elusive.

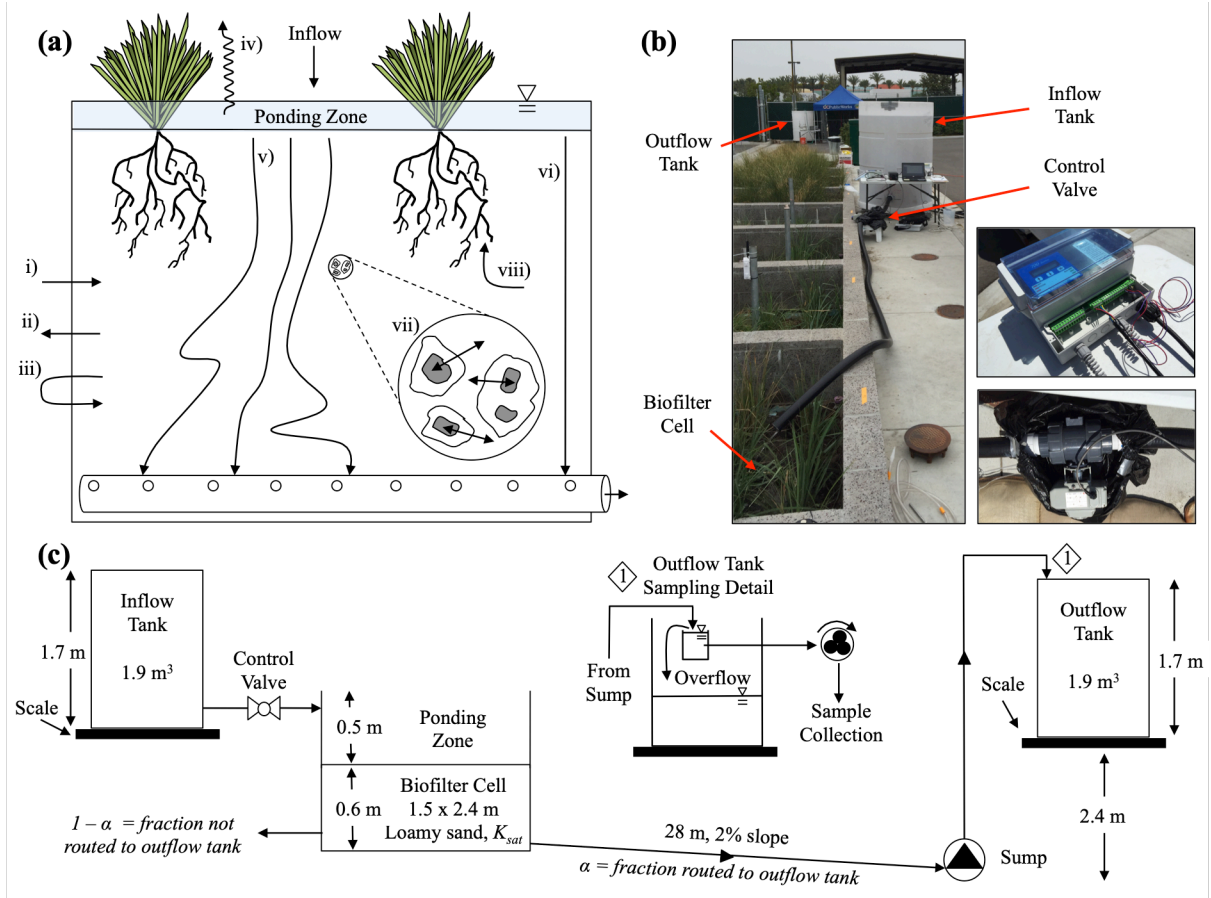


Figure 1. (a) Schematic diagram of transport processes that may influence solute transport through the lined biofilter used in our field experiments, including lateral infiltration and exfiltration with the surrounding soil ((i), (ii) and (iii)); outflow by evapotranspiration, gravitational drainage through the filter media, and short-circuiting ((iv), (v), (vi)); diffusive exchange of water and solutes between pore spaces and micro-porosity within individual grains or organic material (vii), and uptake of water and solutes by plant roots (viii). (b) Photographs of the experimental set-up at the OCPW Low Impact Development Demonstration Facility (left), and the programmable controller and valve (top and bottom right). (c) Detail of the storm simulation experiments, including the vertical and horizontal positions of inflow and outflow tanks, control valve, biofilter test cell, and sampling set-up in the outflow tank (not to scale).

Part of the problem is that transient unsaturated flow imposes severe challenges for predictive modeling. The Richards equation, which describes transient unsaturated flow through porous media, can be solved to estimate time varying flow and saturation through biofilters in

one-, two-, or three-dimensions (e.g., using the numerical package Hydrus (Simunek et al., 2008)). These solutions can be coupled to the advection-dispersion equation (ADE) and one or more hypothesized pollutant removal mechanisms, to estimate pollutant removal in biofilters and analogous vadose zone systems (Massoudieh et al., 2017; Radcliffe & Simunek, 2010; Simunek et al., 2008). While this approach may work well as a theoretical exercise (Alikhani, et al., 2020; dos Santos et al., 2013) and under highly controlled conditions in the laboratory (Al-Mashaqbeh & McLaughlan, 2012; Behroozi et al., 2020; Henrichs et al., 2009; Horel et al., 2015; Saiers and Lenhart, 2003; Trenouth & Gharabaghi, 2015) or field (Boivin et al., 2006; Jiang et al., 2010; Massoudieh et al., 2017), its general application is limited by the information required (boundary conditions, soil hydraulic properties, root profiles, and so on) and the fact that biofilters, like the catchments they are nested within, are “complex, heterogeneous, and poorly characterized by direct measurement” (Kirchner, 2009).

Alternatively, mass balance over a control volume drawn around the biofilter media—so-called “bucket models”—can track the temporal evolution of soil moisture and solutes in these systems. Daly et al. (2012) used a bucket model to derive the probability density of water volume stored in a biofilter based on a stochastic description of rainfall together with biophysical models for gravitational drainage and evapotranspiration (ET). The power of bucket models lies in their simplicity; an enduring challenge has been how to leverage their output into estimates of pollutant removal. Daly et al. (2012) bridged this gap by relating the pore fluid total nitrogen concentration in a biofilter to degree of soil saturation (estimated from the bucket model) on the premise that low saturation levels are associated with “a reduction in nitrogen plant uptake and denitrification with a consequent accumulation of nitrogen in the filter media that is then washed out during the next inflow event.” While clever, this approach does not address the more general

problem of predicting pollutant removal as stormwater passes through a biofilter or other GSI. Further, Daly et al.'s bucket model was implemented at a daily time step, and consequently within-storm processes (such as pollutant breakthrough curves) cannot be resolved. Randelovic et al. (2016) proposed a hybrid approach in which the unsteady water balance is solved with a bucket model while pollutant removal in the filter media and submerged zone is predicted with the one-dimensional ADE coupled with one or more pollutant removal mechanisms. Their framework accurately predicts micropollutant removal in field-scale stormwater biofilters (Randelovic et al., 2016) but at the cost of significant complexity—the model consists of 25 coupled equations and requires the specification of 32 variables. Refinements of this model continue to be published (Shen et al., 2018; Zhang et al., 2019) and incorporated into practice oriented GSI design software (e.g., MUSIC (eWater Ltd., 2020)) (reviewed in Jefferson et al., 2017 and Li et al., 2017).

In this paper we propose and test an entirely new approach for predicting unsteady solute transport through GSI: unsteady transit time distribution (TTD) theory. TTD theory combines the simplicity of bucket models with the temporal resolution and physical insights provided by process-based models of solute fate and transport in transiently unsaturated flow systems. The theory was developed by hydrologists to characterize the myriad transport pathways and timescales associated with water and solute transport through catchments to streams (Rinaldo et al., 2015; Rinaldo et al. 2011) but has since been applied to a diverse array of environmental problems (e.g., Metzler et al., 2018; Smith et al., 2018). In place of a mass conservation equation (such as the ADE), TTD theory is premised on an unsteady conservation equation for the age distribution of water entering, stored in, and leaving a system. These age distributions, in turn, encode all information needed to estimate solute breakthrough concentrations, including the time

history of inflows (e.g., in the case of a biofilter, the magnitude and timing of storm events) and the transformation reactions that occur as water flows through the system along diverse flow paths. In short, TTD theory elegantly links hydrologic processes to water quality outcomes (Hrachowitz et al., 2016).

There are at least two reasons why TTD theory is a potentially important advance over current approaches for modeling pollutant removal in GSI: (1) *parsimony*; and (2) *extensibility*. The unsteady TTD model presented later requires the specification of just one unknown parameter, the effective size of the biofilter (taking lateral exchange of water and solutes with the surrounding soil into account). TTD models can be linked in series and parallel (Bertuzzo et al., 2013; Hrachowitz et al., 2016) to represent GSI networks and hydrological response units (e.g., hillslopes, groundwater, wetlands, rivers) in urban catchments. Thus, TTD theory directly addresses a significant limitation with existing GSI modeling frameworks; namely, their “uncertainty in simulating the propagation of flows through pathways such as stormwater networks, pervious runoff and subsurface flows” (Li et al., 2017).

The paper is organized as follows. We begin by developing the TTD modeling framework needed for GSI applications (Section 2). A field-scale test of the TTD theory is then described (Section 3) followed by experimental and modeling results (Section 4), a discussion of water quality implications (Section 5), and conclusions (Section 6).

2. Modeling Framework

The application of TTD theory to GSI entails three steps: (1) a control volume is drawn around the feature of interest, in our case the soil media component of a biofilter; (2) an unsteady water balance is performed over the control volume, taking into account time-varying inflows, outflows, and change in water storage; and (3) the age distribution of water in the control

volume, and in water leaving the control volume by gravitational drainage and ET, is estimated from TTD theory, along with any water quality metrics (e.g., solute breakthrough curves) of interest. In this section we begin by describing two different approaches for preparing the unsteady water balance, including a simple bucket model (Section 2.1) and a numerical solution of the Richards equation coupled with soil hydraulic functions (Section 2.2). We then solve the age conservation equation (Section 2.3.3) and derive a set of expressions for the age distribution's central tendency and spread (Section 2.3.4) and the breakthrough concentration of a conservative solute (Section 2.3.5).

2.1 Bucket Model Water Balance

Equation (1a) is an unsteady water balance over a control volume drawn around the biofilter media, where the variable t [T] is time and the functions $S(t)$ [L], $J(t)$ [L T⁻¹], $Q(t)$ [L T⁻¹], and $ET(t)$ [L T⁻¹] represent, respectively, the time-varying volume of water in storage, infiltration rate of water into the biofilter from the ponding zone, gravitational discharge of water out of the biofilter, and ET across the top boundary of the biofilter (Daly et al., 2012). All volumes and flows are normalized by the biofilter's surface area.

$$\frac{dS}{dt} = J(t) - Q(t) - ET(t) \quad (1a)$$

$$S(t=0) = S_0 \quad (1b)$$

The initial condition (equation (1b)) stipulates that the area-normalized water in storage at time $t=0$ is $S=S_0$ [L]. To solve equation (1a) we must first specify the storage dependence of all terms on the right-hand side. These are discussed in turn.

2.1.1 Dependence of Infiltration on Storage

For the field experiments described later, the biofilter is lined and outfitted with an underdrain open to the atmosphere. Under these conditions, a parsimonious description of the infiltration

rate can be written as follows, where the variables represent the inflow of stormwater from the surrounding catchment into the ponding zone, $I(t)$ [$L\ T^{-1}$], the biofilter media's average saturated hydraulic conductivity, K_{sat} [$L\ T^{-1}$], and its maximum water storage volume, S_{max} [L] (equal to the biofilter's area-normalized void volume):

$$J(t) = \begin{cases} I(t), & 0 < S(t) < S_{max} \\ K_{sat}, & S(t) = S_{max} \end{cases} \quad (2)$$

This simple expression approximates the three phases of infiltration (Williams et al., 1998) as follows. Infiltration equals inflow during the *Filling Phase*, which begins when stormwater first enters the ponding zone and infiltration is dominated by capillary forces: $S(t) < S_{max}$, $J(t) = I(t)$.

Infiltration equals the saturated hydraulic conductivity during the *Transition Phase* as the biofilter approaches full saturation: $S(t) = S_{max}$, $J(t) = K_{sat}$. During this phase, water level in the ponding zone rises whenever inflow exceeds the media's saturated hydraulic conductivity.

Infiltration is zero during the *Draining Phase*, which commences once inflow has ceased and the ponding zone has drained: $S(t) < S_{max}$, $J(t) = I(t) = 0$. While process-based models of infiltration are available (e.g., Green & Ampt, 1911), equation (2) is consistent with the field observations described later (see Section 4) and its sole variables (K_{sat} and S_{max}) are easily measured biofilter design parameters (Le Coustumer et al., 2012; Le Coustumer et al., 2009; Payne et al., 2015; Peng et al., 2016).

2.1.2 Dependence of Gravitational Discharge on Storage

Kirchner (2009) posited that streamflow out of a catchment can be represented by a single non-linear function of the catchment's water storage, $Q(t) = f(S(t))$. One such functional relationship

derives from the power-law recession model for streamflow where the prefactor, a , and exponent, b , are empirical constants:

$$\frac{dQ}{dt} = -aQ^b \quad (3a)$$

When coupled with an unsteady water balance over the catchment, Kirchner demonstrated that equation (3a) can be manipulated to yield an algebraic expression for streamflow as a function of storage (equation (14) in Kirchner (2009)). Here we adopt a rearranged form of Kirchner's algebraic relationship to describe gravitational discharge from a biofilter (equation 3b), where the new variable, $S_{\min}$ [L], is the residual storage at which all discharge ceases:

$$Q = K_{\text{sat}} \left(\frac{S - S_{\min}}{S_{\max}} \right)^g \quad (3b)$$

The constants appearing in equations (3a) and (3b) are related as follows:

$$a = g K_{\text{sat}}^{1/g} / S_{\max} \quad (3c)$$

$$b = 2 - 1/g \quad (3d)$$

The new variables, $S_{\min}$ and g , are emergent properties of the transient unsaturated flow field; i.e., they must be determined empirically based on experimental observations or numerical solutions of the Richards equation.

2.1.3 Dependence of Evapotranspiration (ET) on Storage

ET also depends non-linearly on water storage, but only when storage falls below a critical value known as the incipient water stress (Allen et al., 1998; Daly et al., 2012). Above the incipient water stress, ET approaches a maximum rate (set by local environmental conditions, including wind speed, vapor pressure deficit, temperature, and plant-specific characteristics) called potential evapotranspiration. While biofilters often operate at or below the incipient water stress

(Hess et al., 2019) this was not the case for the experiments described later, which involved a sequence of back-to-back simulated storms. Accordingly, in this study we approximated ET with an hourly time series of reference crop potential evapotranspiration (cPET) following FAO guidelines (Allen et al., 1998) and based on measurements at, or nearby, the field site together with plant-specific traits (details in Text S1 of the Supporting Information (SI), Appendix B).

2.1.4 Numerical Implementation

The water balance bucket model was solved by substituting into equation (1a) the above expressions for infiltration (equation (2)) and gravitational discharge (equation (3b)), along with hourly estimates of cPET (Section 2.1.3). The model was then forced with timeseries (sampling frequency $\sim 1 \text{ min}^{-1}$) of measured stormwater inflow and numerically integrated (details in Text S2 and Figure S1, SI). These simulations yielded $\sim 1 \text{ min}^{-1}$ timeseries of infiltration, storage and gravitational discharge over the 17 simulated storm events described in Section 3.

2.2 Numerical Solution of the Richards Equation

To calibrate the gravitational discharge expression (equation (3b)) and as a check on the bucket model predictions described above, $\sim 1 \text{ min}^{-1}$ time series of infiltration, storage and gravitational discharge were also simulated with the one-dimensional Richards equation (Hydrus 1D, Version 4.17.0140, PC-Progress, Prague, Czech Republic). The model was forced with measured inflow rates and hourly estimates of cPET (Section 2.1.3). Gravitational discharge from the biofilter's underdrain was represented by a free drainage bottom boundary condition (Jiang et al., 2019).

The depth, porosity, and maximum storage of the biofilter were taken as, respectively, $d_b = 0.6 \text{ m}$, $\theta_s = 0.41$, and $S_{\text{max}} = d_b \theta_s = 0.246 \text{ m}$ (estimated from six cores of the biofilter media collected post-experiment with a 7.6 cm-diameter carbon steel corer). With one exception, we adopted Hydrus 1D's default hydraulic soil parameters for loamy sand (van Genuchten shape parameters

$\alpha_{vg} = 12.4 \text{ m}^{-1}$ and $n_{vg} = 2.28$ [-], residual soil water content $\theta_r = 0.057$ [-], tortuosity parameter $l=0.5$ [-]). The exception was saturated hydraulic conductivity, K_{sat} , which was estimated from measurements of peak discharge and in situ measurements with a modified Philip-Dunne Infiltrimeter (Text S3, SI).

2.3 Transit Time Distribution (TTD) Theory

2.3.1 Solving the Age Conservation Equation

The age distribution of water in the control volume surrounding the biofilter's soil media is governed by the following age conservation equation (Botter et al., 2011; Harman, 2015):

$$\frac{\partial S_T}{\partial t} = J(t) - Q(t)\bar{P}_Q(T,t) - ET(t)\bar{P}_{ET}(T,t) - \frac{\partial S_T}{\partial T} \quad (4a)$$

$$S_T(T,t) = S(t)P_{RTD}(T,t) \quad (4b)$$

$$S_T(T=0,t) = 0 \quad (4c)$$

$$S_T(T,t=0) = S_0 H(T-T_0) \quad (4d)$$

$$H(x) = \begin{cases} 0, & x < 0 \\ 1, & x > 0 \end{cases} \quad (4e)$$

The conservation equation's dependent variable, age-ranked storage $S_T(T,t)$ [L], represents the area-normalized volume of water stored in the biofilter media control volume at any time t with ages T or younger. Age-ranked storage is defined mathematically as the product of the area-normalized volume of stored water, $S(t)$, and the cumulative distribution function (CDF) for the fraction of that stored water with ages less than or equal to T ; i.e., the stored water's residence time distribution (RTD), $P_{RTD}(T,t)$ (equation (4b)). As the age variable, T , becomes large, the RTD's CDF tends to unity and the age-ranked storage function collapses to the area-normalized

volume of water in storage: $S_T(T \rightarrow \infty, t) = S(t)$. The boundary condition (equation (4c)) ensures that no water stored in the control volume has an age less than $T=0$. The initial condition (equation (4d)) implies that, at time $t=0$, the volume of “original” water in storage, S_0 , has a single age, $T=T_0$, where the Heaviside function is denoted by $H(x)$ (equation (4e)). As applied to biofilters, equation (4a) equates the change of age-ranked storage of water in the biofilter media (left-hand side) to the infiltration of stormwater of age $T=0$ (first term on right-hand side); outflow of water by gravitational discharge (second term) and ET (third term) with age distributions $\bar{P}_Q(T, t)$ and $\bar{P}_{ET}(T, t)$, respectively; and aging of water in storage (fourth term).

The two CDFs appearing in the outflow terms, $\bar{P}_Q(T, t)$ and $\bar{P}_{ET}(T, t)$, represent the fraction of water leaving the biofilter as gravitational discharge and ET with ages T or less at time t . The backward arrows on these CDFs indicate they are “backward TTDs”; i.e., they represent the age distribution of water *leaving* the biofilter at time t . A corresponding set of “forward TTDs” can be written for the life expectancy of water parcels entering the biofilter at time, t_i . The relationship between forward and backward TTDs is given by Niemi’s Theorem (Benettin et al., 2015a; Harman, 2015; Niemi, 1977). Under unsteady conditions and depending on the nature of the storage selection function (see next section), the backward TTDs for gravitational discharge and ET are not necessarily equal, nor are they necessarily equal to the RTD of water in storage (Botter et al., 2011).

2.3.2 Ranked StorAge Selection (SAS) Function

As written, equation (4a) is mathematically ill posed because it consists of a single equation with three unknown functions: $S_T(T, t)$, $\bar{P}_Q(T, t)$, and $\bar{P}_{ET}(T, t)$. This closure problem can be resolved by introducing a new CDF, the ranked StorAge Selection (SAS) function, $\Omega(S_T, t)$ [-], which maps

the fraction of outflow with ages less than or equal to T (i.e., the CDF form of the backward TTD for discharge or ET) to the fraction of age-ranked water in storage with that age or younger “selected” for outflow by either gravitational drainage or ET (Botter et al., 2011; Harman, 2015):

$$\bar{P}(T, t) = \Omega(S_T(T, t), t) \quad (5a)$$

In principle, the functional form of the SAS function can be calculated by averaging the ADE for solute transport over the control volume (Benettin et al., 2013; Rinaldo et al., 2015). For the purposes of this study, however, we adopted a “uniform SAS” function, under the assumption that water in storage has an equal probability of being selected for outflow regardless of its age (Harman, 2015):

$$\Omega_Q(S_T, t) = \Omega_{ET}(S_T, t) = S_T(T, t) / S(t), \quad S_T(T, t) \in [0, S(t)] \quad (5b)$$

Uniform SAS functions often apply to systems, such as ours, that are far from well-mixed (Bertuzzo et al., 2013; Benettin et al., 2013; Benettin et al., 2015b; Danesh-Yazdi et al., 2018; Kim et al., 2016; Rodriguez et al., 2018).

2.3.3 Exact Solution for Age-Ranked Storage under Uniform Selection

Under uniform sampling, the age conservation equation (equation 4a) can be solved exactly for certain choices of initial and boundary conditions (Botter et al., 2011; Bertuzzo et al., 2013).

Equation (6a) is one such solution that satisfies the initial and boundary conditions presented earlier (equations (4c) and (4d), see Text S4 (SI) for derivation); the superscript “U” denotes that the solution is premised on the choice of a uniform storage selection function.

$$S_T^U(T, t) = e^{-\bar{J}_Q(t) - \bar{J}_{ET}(t)} \left[S_0 H(T - t - T_0) + \int_w^t e^{\bar{J}_Q(v) + \bar{J}_{ET}(v)} J(v) dv \right] \quad (6a)$$

$$w = \begin{cases} 0, & T - t \geq 0 \\ t - T, & T - t < 0 \end{cases} \quad (6b)$$

$$\bar{f}_Q(v) = \int_0^v \frac{Q(u)}{S(u)} du \quad (6c)$$

$$\bar{f}_{ET}(v) = \int_0^v \frac{ET(u)}{S(u)} du \quad (6d)$$

According to equation (6a) age-ranked storage (left-hand side) is influenced by the evolving age distribution of both “original” water in storage at time $t = 0$ (first term on right-hand side) and “young water” that infiltrates during storm events (second term). This solution was numerically integrated (details in Text S4 (SI)) to yield $\sim 1 \text{ min}^{-1}$ timeseries of age-ranked storage in the biofilter, after substituting bucket model simulations for infiltration, $J(t)$, storage, $S(t)$, and gravitational discharge, $Q(t)$ (Section 2.1).

2.3.4 Age Structure of Stored Water in the Biofilter

Under uniform selection the backward TTDs for gravitational discharge and ET are equal, and equal to the RTD of water in storage (compare with equation (4b)) (Harman, 2015):

$$P_{\text{RTD}}(T, t) = \bar{P}_Q(T, t) = \bar{P}_{ET}(T, t) = \frac{S_T(T, t)}{S(t)} = \frac{e^{-\bar{f}_Q(t) - \bar{f}_{ET}(t)}}{S(t)} \left[S_0 H(T - t - T_0) + \int_w^t e^{\bar{f}_Q(v) + \bar{f}_{ET}(v)} J(v) dv \right] \quad (7a)$$

The 5th, 50th, and 95th percentile ages of water in storage and outflow at any time, t , can be obtained from equation (7a) by numerically solving the following implicit equations for water age: $S_T(T_{0.05}, t)/S(t) = 0.05$, $S_T(T_{0.5}, t)/S(t) = 0.5$, and $S_T(T_{0.95}, t)/S(t) = 0.95$. The age-ranked storage’s probability density function (PDF) can be calculated from equation (7a) by differentiation where the symbol δ denotes the Dirac delta function:

$$p_{\text{RTD}}^U(T, t) = \bar{p}_Q^U(T, t) = \bar{p}_{ET}^U(T, t) = \frac{\partial P_{\text{RTD}}^U}{\partial T} = \delta(t + T_0 - T) \frac{S_0}{S(t)} e^{-\bar{f}_Q(t) - \bar{f}_{ET}(t)} + H(t - T) \frac{J(t - T)}{S(t)} e^{-\bar{f}_{ET}(t) + \bar{f}_{ET}(t - T) - \bar{f}_Q(t) + \bar{f}_Q(t - T)} \quad (7b)$$

The mean age in storage and outflow immediately follows by taking the first moment of the PDF for age-ranked storage:

$$\mu_{\text{RTD}}^U(t) = \mu_Q^U(t) = \mu_{\text{ET}}^U(t) = \int_0^\infty v p_{\text{RTD}}^U(v, t) dv = \frac{1}{S(t)} \left[S_0 e^{-\bar{f}_Q(t) - \bar{f}_{\text{ET}}(t)} (t + T_0) + \int_0^t (t - u) J(u) e^{-\bar{f}_{\text{ET}}(t) + \bar{f}_{\text{ET}}(u)} e^{-\bar{f}_Q(t) + \bar{f}_Q(u)} du \right] \quad (7c)$$

Further details on the derivation and numerical implementation of equations (7b) and (7c) are described in Text S5 (SI).

2.3.5 A TTD Theory for Solute Fate and Transport through a Biofilter

The concentration of a non-reactive and non-adsorbing (i.e., conservative) solute in water leaving the biofilter by gravitational discharge, $C_Q(t)$, can be calculated by convolving the PDF of the backward TTD (equation (7b)) with the concentration of solute, $C_J(t_i, T)$, that entered the biofilter at time, $t_i = t - T$, and exited the biofilter as gravitational discharge at time t and age T (Harman, 2015):

$$C_Q(t) = \int_0^t C_J(t - T, T) \bar{p}_Q(T, t) dT \quad (8a)$$

Despite its simplicity, this convolution integral incorporates a rich set of processes, including unsteadiness in the biofilter's water balance (e.g., time-varying inflows, outflows, and storage, encoded through the time-evolution of the backward TTD) and unsteadiness in the solute concentration entering the biofilter from the ponding zone (through the dependence of $C_J(t_i, T)$ on the inflow time, $t = t_i$) (Harman, 2015). Combining equations (7b) and (8a), we arrive at the following solution for the concentration of a conservative solute in water discharged from the biofilter, where C_0 is the concentration of solute present in the original water stored in the biofilter at time, $t = 0$:

$$C_Q(t) = C_0 \frac{S_0 e^{-\bar{f}_Q(t) - \bar{f}_{ET}(t)}}{S(t)} + \frac{1}{S(t)} \int_0^t C_J(u) J(u) e^{-\bar{f}_{ET}(t) + \bar{f}_{ET}(u) - \bar{f}_Q(t) + \bar{f}_Q(u)} du \quad (8b)$$

For the experiments described later, a subset of 17 simulated storms were tagged with bromide, which we assumed behaved conservatively (Levy & Chambers, 1987). The inflow concentration for these storms can be expressed as follows, where $C_{J,m}$, $t_{m,s}$, and $t_{m,e}$ are the m -th storm's bromide concentration, start time and end time, respectively, and the sum is taken over all N storms:

$$C_J(t_i) = \sum_{m=1}^N C_{J,m} H(t_i - t_{m,s}) H(t_{m,e} - t_i) \quad (9a)$$

Substituting equation (9a) into equation (8b), setting $C_0 = 0$ (because, in our experiments, no bromide was present in the biofilter's original water), and using the distributive property of integration, we arrive at the following expression for bromide concentration in water leaving the biofilter by gravitational discharge (details in Text S6 (SI)):

$$C_Q(t) = \frac{1}{S(t)} \sum_{m=1}^N C_{J,m} H(t - t_{m,s}) \int_{t_{m,s}}^y J(u) e^{-\bar{f}_{ET}(t) + \bar{f}_{ET}(u) - \bar{f}_Q(t) + \bar{f}_Q(u)} du \quad (9b)$$

$$y = \begin{cases} t, & t < t_{m,e} \\ t_{m,e}, & t \geq t_{m,e} \end{cases} \quad (9c)$$

In deriving equation (9b) we have assumed that plants in the biofilter take up bromide and water in the same proportion, which may not be the case in practice (e.g., if a solute is excluded from plant uptake its pore fluid concentration will increase over time by in situ evaporative concentration (Bertuzzo et al., 2013; Harman, 2015)). However, in the field experiments described later (Section 4) ET represents a very small portion of the overall water balance and hence in situ evaporative concentration can be neglected in our case. Time series ($\sim 1 \text{ min}^{-1}$) of

bromide breakthrough concentration were simulated with equation (9b) following the numerical procedures described in Text S6 (SI).

3. Field Methods

3.1 Orange County Public Works (OCPW) Biofilter Test Facility

Field-scale biofilter challenge experiments were carried out at the Orange County Public Works (OCPW) low impact development demonstration facility located in the City of Orange, Orange County, California. Experiments were conducted in a biofilter test cell (approximately 2.4 m x 1.5 m x 0.6 m deep) built by a local contractor with previous GSI construction experience (Tobo Construction, Figure 1b). The test cell, which was lined and outfitted with an underdrain, consisted of a concrete slab floor and four cinderblock walls extending approximately 0.5 m above the filter media surface to create a ponding zone (Figures 1b, 1c). The filter media consisted of sand (65%), sandy loam (20%), and compost (15%) (v/v basis). In January 2017, the media was planted with a European grey sedge, *Carex divulsa tumulicola*. When we conducted our first set of experiments in June 2018 the plant community also included opportunist ruderal weed species (e.g., the common dandelion). While our biofilter is open to the atmosphere, no measurable rainfall occurred during the set of experiments described below.

The research team retrofitted the biofilter with an upstream 1890 L “inflow” tank (Custom Roto-Molding, Inc., Caldwell, ID) which drained by gravity through a programmable control valve (Sigma Controls, Inc., Perkasi, PA) to the biofilter’s ponding zone (Figure 1b). The weight of the inflow tank was monitored continuously at ~10 Hz (WinWedge, TAL Technologies Inc., Philadelphia, PA) with a calibrated industrial scale (PCE-SW 3000N Pallet Scale, PCE Americas Inc., Jupiter, FL). The weight measurements were lowpass filtered (Davis, 2002), differentiated, and divided by the density of water to yield $\sim 1 \text{ min}^{-1}$ estimates for the

volumetric discharge of water entering the ponding zone (these measurements correspond to the inflow term, $I(t)$, in equation (2)). Following the experiments conducted in the summer of 2018 we discovered that, during construction, a ca., 5 cm diameter hole had been drilled through the base of the cinderblock wall separating our test cell from the adjacent test cell (and through the wall separating the adjacent test cell from the next test cell and so on) to accommodate a buried irrigation pipe. A substantial fraction of stormwater added to our test cell (approximately 50%) laterally exfiltrated to the adjacent cell through this hole. While not part of our original design, this feature made for a more realistic field experiment, as most operational biofilters undergo at least some degree of subsurface exfiltration (e.g., Brown & Hunt, 2011). Indeed, our exfiltration rate of ~50% is close to the stormwater volume reduction design goal for GSI of 67% (Davis, 2008). To account for lateral exfiltration, gravitational discharge estimated from the bucket model (Section 2.1) was routed as follows. A fixed fraction, α , was assigned to the underdrain and the rest, $1-\alpha$, to lateral exfiltration to the adjacent test cell (Figure 1c). The fraction α was estimated using several independent experimental methods (see Text S7 and Figure S6, SI).

Water exiting the biofilter through the underdrain flowed by gravity through a buried manifold to an underground sump and from there was periodically pumped (Model 98 Sump Pump, Zoeller Pump Company, Louisville, KY) up to an “outflow” tank sitting on a calibrated industrial scale at ground level (identical to the inflow tank set up, Figure 1c). A timeseries ($\sim 1 \text{ min}^{-1}$) of volumetric discharge entering the outflow tank was estimated from high frequency (10 Hz) measurements of the tank’s weight following the same procedure described above for the inflow tank (corresponding to the $Q(t)$ term in equations (1a) and (3b)). Time series of volumetric discharge and bromide concentration measured at the outflow tank were time-shifted

backwards by 60 minutes to account for the transit of water from the biofilter's underdrain to the outflow tank and the overly fast response of the bucket model to storm events (Text S8, SI).

3.2 Experimental Storm Hydrograph

Municipal separate storm sewer system (MS4) permit requirements for the Santa Ana Region (where our experiments were carried out) stipulate that new development and significant re-development projects include stormwater control measures sufficient to capture runoff volume generated by the 85th percentile storm, which at this field site corresponds to 2.1 cm of stormwater depth (volume per unit catchment area) over a 24-hour period (OCPW, 2017). With this regulatory requirement in mind, we designed our experimental storm hydrograph as follows: (1) seven 24-hour rainfall events were selected from measurements at an onsite rain gauge over the years 2011 to 2016; (2) an average hyetograph was constructed from these seven events after aligning peaks and standardizing the total 24-hour rainfall depth to 2.1 cm; and (3) a design storm hydrograph was calculated from the average hyetograph by the Rational Method (Brooks et al., 2013) assuming a unit runoff coefficient (corresponding to 100% imperviousness) and a catchment area of 82.3 m². The corresponding biofilter-to-catchment area ratio (4.5%) is typical for urban landscapes in Southern California (Ambrose & Winfrey, 2015). The design storm hydrograph was subsequently programmed into the control valve to regulate the flow of water into the biofilter's ponding zone during each simulated storm (Figure 1b) (see Text S9 and Figure S8 (SI) for a comparison of measured and design storm hydrographs).

3.3 Bromide Tracer Experiments

A sequence of simulated experimental storms (each of which conformed to the storm hydrograph described in Section 3.2) were discharged to our experimental biofilter over a five-day period in the summer of 2018 (June 25-29) and again over a five-day period in the summer of 2019 (June

1-5). Ten storms were simulated in 2018, one in the morning and another in the afternoon on each day. The afternoon storms were spiked with bromide (final concentration $\sim 50 \text{ Br}^- \text{ mg/L}$) while the morning storms were bromide free. The storm sequence in 2019 consisted of: (1) two bromide-free storms on the first day, one in the morning and one in the afternoon; (2) two days later a single bromide-spiked storm in the morning (final concentration of $124 \text{ Br}^- \text{ mg L}^{-1}$); and (3) over the following two days two bromide-free storms per day, one in the morning and one in the afternoon. Three replicate 40 mL samples were collected from the inflow tank before each simulated storm. Outflow samples were collected as follows. Water entering the outflow tank from the sump was directed into a continuously overflowing 5 L bucket affixed to the top of the tank (the bucket overflowed into the tank, see Figure 1c). Water in the bucket was continuously sub-sampled (20 mL min^{-1}) by means of a peristaltic pump (BioLogic LP, Bio-Rad, Hercules, CA) and fractionated into 50 mL conical tubes (Falcon, Corning Life Sciences, Tewksbury, MA) according to a pre-defined sampling schedule (2018: every 2, 5, or 10 minutes, with more rapid sampling during the first hour of biofilter outflow; 2019: every 5 minutes) (inset, Figure 1c). During each storm, outflow samples were collected in this manner until the on/off cycling of the sump pump fell below $1/30 \text{ min}^{-1}$. The bromide concentration in each sample was measured by ion chromatography (2018: 940 Professional IC Vario, Metrohm AG, Herisau, Switzerland; 2019: Dionex DX-120, Thermo Fisher Scientific, Waltham, MA). A total of $N=30$ (15) and 435 (147) inflow and outflow samples, respectively, were analyzed during the 2018 (2019) experiments.

In addition to the timing of storm events and the periodic (2018) and non-periodic (2019) nature of the bromide dosing, the 2018 and 2019 experiments differed in several other respects (details in Text S9, SI), including: (1) the nature of the water used (tap water in 2018 and either

stormwater alone or a 50:50 stormwater and raw sewage mixture in 2019); (2) the partial sealing of the hole in the test cell wall after 2018; (3) operation of the control valve (automatically and manually actuated in 2018 and 2019, respectively); and (4) change in plant community from a European grey sedge and ruderal weeds in 2018 to a native southern California sedge in 2019.

4. Results and Discussion

4.1 Lateral Exfiltration and the Effective Volume of the Biofilter

Each experimental storm discharged roughly the same volume of water (1400 to 1500 L) to the biofilter's ponding zone over one to two hours. The volume of water captured in the outflow tank varied by storm, from 378 to 751 L (25 to 49% of the inflow volume) for the ten experiments conducted in 2018, and from 266 to 654 L (21 to 46% of the inflow volume) for the seven experiments conducted in 2019 (Table S1, SI). Across all 17 storms, ET was a minor component of the water budget ($< 0.3\%$ of the ~ 1400 L added per storm, Table S1, SI). Thus, the difference between these inflow and outflow volumes either went to increasing storage or lateral exfiltration to the adjacent test cell (see Text S7, SI).

The fraction of inflow volume recovered at the outflow tank is inversely correlated with antecedent dry period ($R^2=0.82$, Figure S6, SI), consistent with the hypothesis that at least some of the unrecovered water goes to storage. Extrapolating the fractional water recovery back to an antecedent dry period of zero hours (under the premise that the change in storage should be zero in this case) we estimate that, in both 2018 and 2019, approximately $\alpha = 46\%$ of the water added to the biofilter is routed to the outflow tank while $1-\alpha = 54\%$ is lost to lateral exfiltration (Text S7, SI). These results are consistent with loss rates we independently measured under steady-state flow conditions (Text S7, SI) and the observed wetting of biofilter media in the adjacent test cell (data not shown), along with previously published modeling studies (Browne et al.,

2008; Lee et al., 2015) and field measurements (Winston et al., 2016) that indicate exfiltration is a dominant mechanism for water volume reduction in GSI. At our site, some of the exfiltrated water and solute may eventually find its way back to the outflow tank, for example by recirculating back through our biofilter test cell (mechanism (iii), Figure 1a) or transiting along another subsurface route to the buried collection manifold (indeed, the test cell adjacent to our biofilter also had an underdrain that could have contributed flow and solute to the manifold and, ultimately, to the outflow tank). Thus, exfiltration can potentially increase the effective volume of our biofilter during solute transport. We return to this idea in Section 4.4.

4.2 Power-Law Model for Gravitational Discharge

Kirchner's power-law model for gravitational discharge (equation (3b)) could not be evaluated from our inflow and outflow measurements, because lateral exfiltration precluded accurate estimates of the gravitational discharge and water storage terms of the equation. Instead, hourly time series for these two quantities were numerically simulated, with Hydrus 1D, over the seventeen experimental storms in 2018 and 2019 (Section 2.2). Consistent with Kirchner's power-law relationship, when normalized and plotted on a log-log basis, the Hydrus-generated time series of discharge and storage collapse to a single line for $Q(t) > 0.05K_{\text{sat}}$ (Figure 2).

Inferred values of the power-law exponent and minimum storage are the same, within error, across both years (2018: $g = 4.99 \pm 0.01$ and $S_{\text{min}} = -3.6 \times 10^{-20} \pm 1.9 \times 10^{-4}$ m; 2019: $g = 5.00 \pm 0.01$ and $S_{\text{min}} = -3.4 \times 10^{-21} \pm 2.2 \times 10^{-4}$ m). This result indicates these parameters are robust to changes in the sequence and length of antecedent dry periods as well as to changes in saturated hydraulic conductivity (within each simulated storm sequence, the saturated hydraulic conductivity declined over time, see Text S3, SI). Substituting $g=5$ into equation (3d) yields a recessionary

exponent of $b=1.8$, which is toward the flashy end of the allowable range, $b \in [1, 2]$ (Kirchner, 2009), consistent with the small storage volume of the biofilter. Our inferred value for the power-law exponent is also concordant with exponent values inferred by Bertuzzo et al. (2013) for gravitational drainage from the vadose zone of a 46 km² catchment in Switzerland (compare $g=5$ with the posterior distribution for the exponent c in their Figure 4).

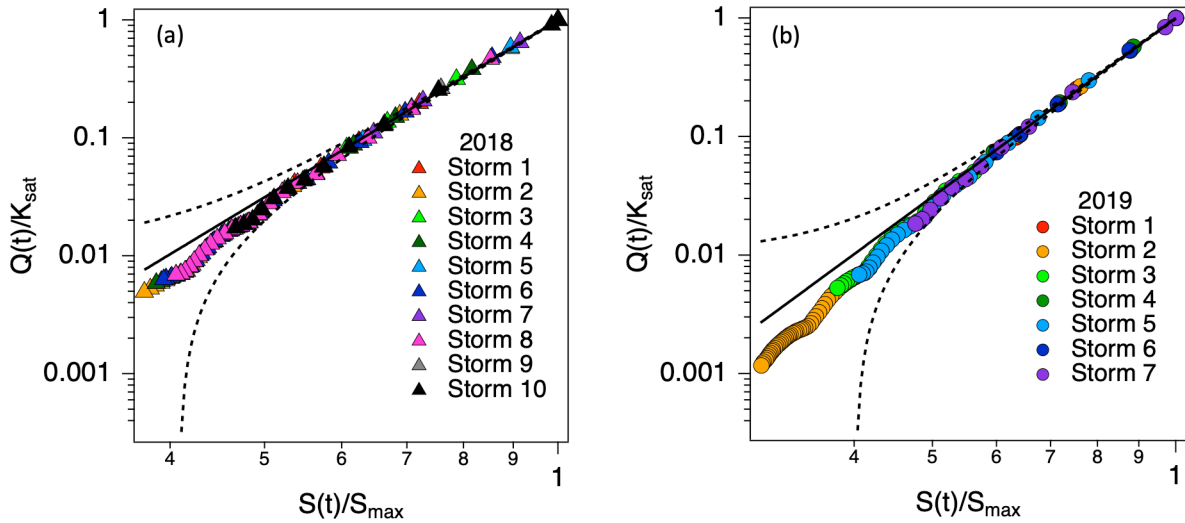


Figure 2. Power-law dependence of gravitational discharge on water storage simulated with Hydrus 1D for storm sequences in (a) 2018 and (b) 2019. Solid and dashed black curves indicate model fit and 95% prediction intervals, respectively.

On the other hand, the inferred value for minimum storage, $S_{min}=0$, is at odds with the expectation that some residual water (e.g., equal to the area normalized volume of water in the biofilter media at field capacity (Hillel, 2003)) should be present in the biofilter following the cessation of gravitational discharge. Two points are relevant here. First, for the set of Hydrus 1D simulations used in the inference step, water storage in the biofilter never fell below the soil media's field capacity due to the large volume of water associated with each storm (compared to

the biofilter's void volume) and the back-to-back nature of the storm sequences in 2018 and 2019 (Section 4.1). Thus, one plausible explanation for the inferred value, $S_{\min}=0$, is that the biofilter was never dry enough to observe an influence of minimum storage on gravitational discharge. Second, the inferred value of the power-law exponent, $g=5$, implies that discharge declines very rapidly with storage. For example, substituting $g=5$ and $S_{\min}=0$ into equation (3b) we predict that gravitational discharge will be $\leq 0.05\%$ of the media's saturated hydraulic conductivity ($Q \leq 0.0005 * K_{sat}$) when storage falls below the media's field capacity ($S < S_{fc} = 0.054$ m for our biofilter). Put another way, the large power-law exponent ensures that there will be very little gravitational discharge once storage drops below field capacity, even if the minimum storage is set to zero. For this reason and consistent with other field applications of equation (3b) (e.g., Bertuzzo et al., 2013), we adopted the inferred value, $S_{\min}=0$, in the bucket model and TTD simulations presented below.

4.3 Unsteady Water Balance: Bucket Model and Hydrus 1D Predictions

Over the 17 experimental storms conducted during 2018 and 2019, numerical solutions of the bucket model (equation (1a)) closely track Hydrus 1D simulations of ponding depth, degree of biofilter saturation, and gravitational discharge (Figure 3). The predicted range of ponding depths (from 0 to 0.2 m above the surface of the biofilter media) is consistent with our field observations and the predicted gravitational discharge rates closely match measurements at the outflow tank (light blue curves, bottom panels of Figures 3a and 3b).

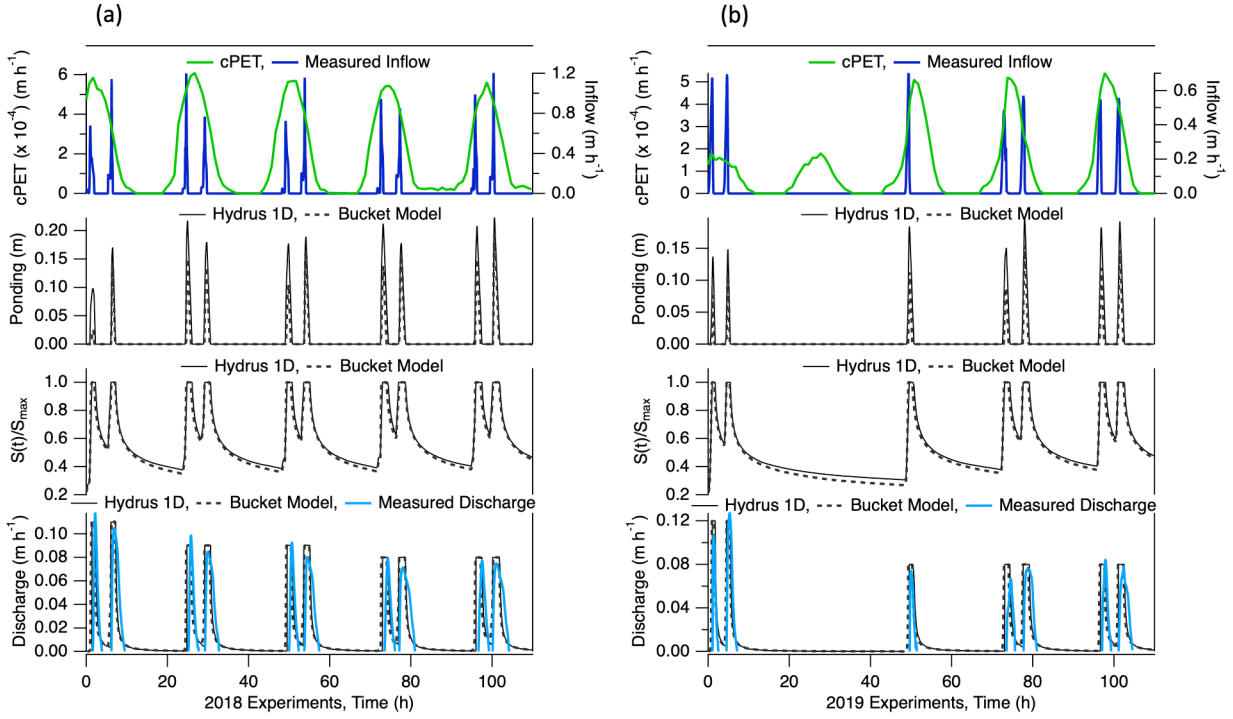


Figure 3. Two approaches for simulating the unsteady water balance in our biofilter: numerical solutions to the Richards equation (Hydrus 1D, solid black curves) and a bucket model (dashed black curves). Colored lines represent measured inflow (dark blue), measured outflow (light blue) and calculated cPET (green) for the set of experiments conducted during the summers of (a) 2018 and (b) 2019. To compare simulated and measured discharge, the former was multiplied by $\alpha = 0.46$ (to account for the fraction of water that is laterally exfiltrated) and the latter was backward time shifted by 60 min.

4.4 TTD Theory Predictions for Bromide Transport

In 2018, our semi-periodic study design consisted of a bromide-free “flushing” storm in the morning (orange arrows in Figure 4a) and a bromide-spiked “tracer” storm in the afternoon (black arrows in Figure 4a) of each day. By the second day of the storm sequence, the normalized bromide breakthrough curves (BTCs) settled into a periodic pattern, oscillating between $c_q/c_{j,1} \approx 0.3$ and 0.6 during the morning and afternoon storms, respectively (black dots in lower graph, Figure 4a). Here, the variable $c_q(t)$ represents the measured bromide concentration at the outlet tank and the variable $c_{j,1} = 48.7 \text{ mg L}^{-1}$ represents the initial bromide

concentration measured in the first afternoon tracer storm (across all five tracer storms the initial bromide concentrations were $c_{j,m} = 48.7, 48.8, 49.3, 48.3,$ and 44.4 mg L^{-1}). The bromide BTC predicted by TTD theory also follows a periodic pattern (solid curve, bottom graph, Figure 4a), but the model consistently under- and over-predicts measured bromide concentrations in the morning and afternoon storms, respectively. These model predictions were calculated from equation (9b) after specifying the timing and initial bromide concentrations associated with each bromide-spiked storm, and running bucket model simulations for $J(t)$, $S(t)$, and $Q(t)$ after setting the maximum storage term (see equation (3b)) equal to the void volume of the biofilter, $S_{\max} = 0.246 \text{ m}$.

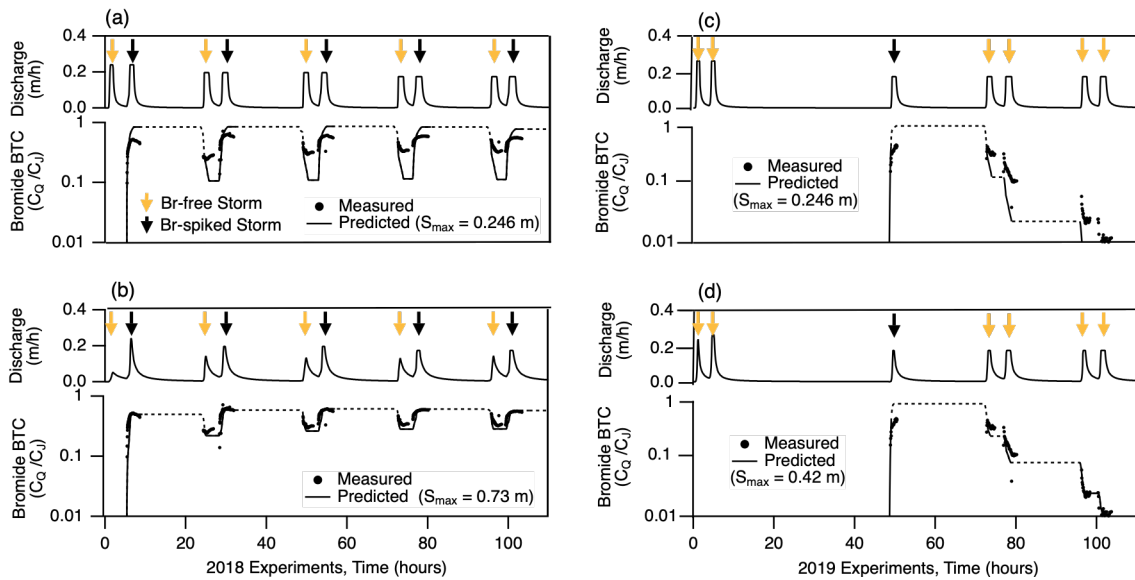


Figure 4. Comparison of measured (points) and predicted (solid and dashed curves) bromide breakthrough curves (BTCs) for the 2018 ((a) and (b)) and 2019 ((c) and (d)) experiments. Model predictions assume $S_{\max}$ equals the physical volume of the biofilter ((a) and (c)) or a volume obtained by fitting the model to the second storm of 2018 (b) or the fourth, fifth, sixth, and seventh storms of 2019 (d). Dashed curves correspond to times when no samples were collected. Vertical arrows mark the bromide-spiked (black) and bromide-free (orange) storms. Each panel also includes bucket model predictions for gravitational discharge given the value of $S_{\max}$ shown.

The TTD model's tendency to overshoot bromide measurements implies it is oversampling young water; i.e., the predicted bromide BTC contains too much bromide-free water during the bromide-free morning storm, and too much bromide-spiked water during the bromide-spiked afternoon storm. One possible explanation for this result is that the uniform storage selection function, which underpins our model (see equation (9b) and discussion thereof), oversamples young water for gravitational discharge. Alternatively, the storage selection function is fine but there is not enough old water in storage to select from. While the former explanation cannot be ruled out (indeed, the science of selecting SAS functions is an active area of current research (Harman, 2019)), the latter explanation is compelling for several reasons. First, the void volume of our biofilter (~900 L) is less than the volume of water flowing into the biofilter with each experimental storm (~1400 L). Therefore, as far as the model is concerned, our biofilter has very limited capacity to store older water from penultimate and older storms. Second, a substantial fraction (>50%) of the inflow volume leaves our biofilter by lateral exfiltration. As noted in Section 4.1, some of this exfiltrated water may eventually return to the outflow tank and thereby increase the effective volume that solutes experience as they transit through the system.

To test the last hypothesis—that the effective volume for solute transport is larger than the biofilter's physical volume—we split the measured bromide data from 2018 into a calibration period (the first bromide-spiked storm, storm #2) and a validation period (all other storms). We then inferred a value of the biofilter's void volume by minimizing the root-mean square error (RMSE) over the calibration period (Figure S9, SI). The optimal volume thus obtained ($S_{\max}=0.73$ m, RMSE=0.041) is about two times larger than the physical volume of the biofilter ($S_{\max}=0.246$ m) consistent with the hypothesis that a substantial fraction of the water that

exfiltrated into the adjacent biofilter test cell eventually returned to the outflow tank. When the inferred value of $S_{\max}=0.73$ m is substituted back into the bucket model and the hydrologic water balance is recomputed, equation (9b) closely tracks the bromide BTC over the validation period (storms #3 through #10, bottom graph in Figure 4b).

Application of TTD theory to the 2019 storm sequence yields similar results. If the maximum volume of the biofilter is set equal to its physical volume ($S_{\max}=0.246$ m), equation (9b) consistently under-predicts bromide breakthrough during the four bromide-free flushing storms (storms #4, 5, 6, and 7, bottom graph in Figure 4c). However, when the effective volume is raised to $S_{\max}=0.42$ m (obtained by minimizing the RMSE for storms #4 through 7, see Figure S9, SI; RMSE=0.31) the model's performance improves markedly (Figure 4d). The void volume inferred from the 2018 experiments ($S_{\max}=0.73$ m) is about 74% larger than the void volume inferred from the 2019 experiments ($S_{\max}=0.42$ m), perhaps reflecting changes in the biofilter test cell over the two years; e.g., after the 2018 experiments the hole at the base of the test cell was partially sealed and the media was replanted (see Text S9, SI and discussion in Section 5.4 below).

5. Implications for Age Structure and Pollutant Removal

5.1 Age Distribution of Water Leaving the Biofilter by Gravitational Discharge

By selecting a uniform SAS function for our model (Section 2.3.2), the backward TTDs for gravitational discharge and ET are equal to the RTD of water stored in the biofilter. Thus, under uniform storage sampling, the age distribution of water in storage is equal to the age distribution of water leaving the biofilter as gravitational discharge.

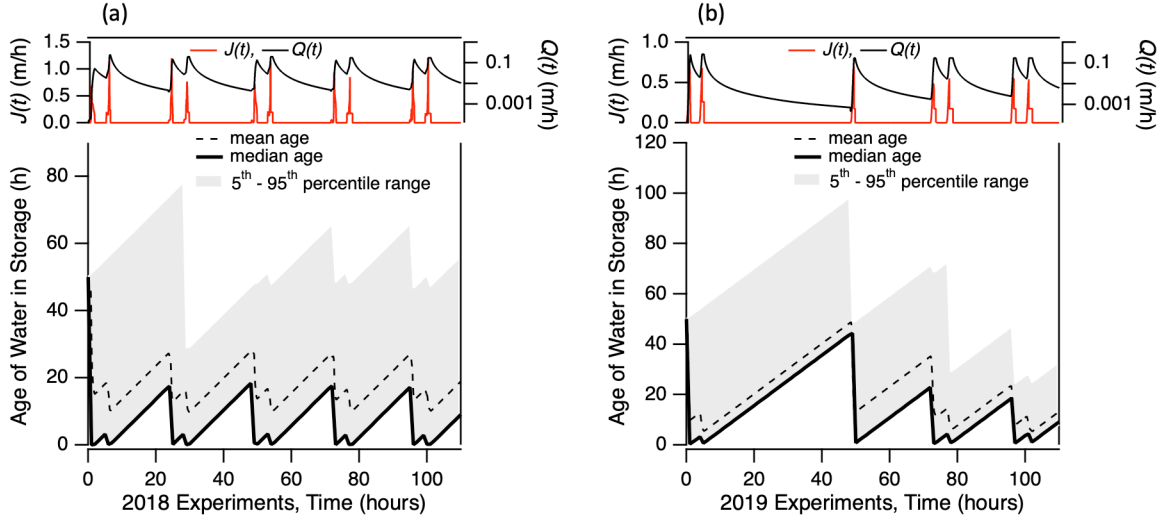


Figure 5. The evolution of mean and median water ages in the biofilter during the sequence of storms in (a) 2018 and (b) 2019. Also shown are the 5th to 95th percentile range (grey band). Top panels indicate the infiltration (red curve) and gravitational discharge (black curve) rate for each storm sequence. For these simulations, we adopted inferred values of maximum storage: $S_{\max} = 0.73$ and 0.42 m for 2018 and 2019, respectively. The age of original water was arbitrarily set to $T_0 = 50$ h and its volume was taken as the product of initial moisture content ($s_0 = 0.22$, corresponding to field capacity) and maximum storage:

$$S_0 = s_0 S_{\max}.$$

During the 2018 experiments, predictions for the median age of water stored in the biofilter (equation (7a) and discussion thereof) follows a semi-periodic pattern, increasing linearly with time between storms (as water stored in the biofilter ages) and rapidly declining to near zero during storm events (as incoming stormwater, of age $T = 0$ h, fills the biofilter, Figure 5a). The 5th and 50th (median) age percentiles overlap but the 95th age percentile is much older, indicating that the age distribution is positively skewed (Ang & Tang, 2007). The 5th and 50th percentiles overlap because, at any time t , more than 50% of water stored in the biofilter is from the most recent storm with an age roughly equal to the antecedent dry period. The 95th percentile age is much older because the rest of water in storage (i.e., water not from the last storm) is from penultimate and earlier storms.

For the simulations presented in Figure 5a we arbitrarily set the initial age of “original” water (i.e., water that was initially present in the biofilter at time, $t=0$) at $T_0=50$ h. Until the fourth storm, this original water constituted more than 5% of water stored in the biofilter, as evidenced by the upward slope of the grey band in Figure 5a (the upward slope reflects the fact that that original water in storage is aging linearly with time). After the fourth storm, the original water’s contribution to storage drops below 5%, as evidenced by a steep drop in the 95th percentile around $t=28$ h (Figure 5a). Thus, four storms were required to flush out 95% of the original water, even though more than 50% of water in the biofilter, at any given time, is from the last storm. A similar pattern is evident for the set of experiments conducted in 2019 (Figure 5b). Across both years the mean age is 5 to 20 hours older than the median age, consistent with a positively skewed age distribution (Ang & Tang, 2007).

5.2 Mapping out the Contribution of Past Storms to Present Storage

TTD theory also allows us to determine the relative contribution of all past storms to water stored in a biofilter at any time, t . If the n -th storm begins at time, $t=t_{b,n}$, then the fraction, $f_n(t)$ [-], of water in storage with that age or younger can be estimated from the RTD’s CDF (see Section 2.3.4) (Kirchner, 2016; Benettin et al., 2017; Lutz et al., 2018):

$$f_n(t) = P_{\text{RTD}}^U(T=t-t_{b,n}, t), \quad t > t_{b,n} \quad (10)$$

We applied equation (10) to all seven storms simulated in 2019, along with the original water present in the biofilter at time, $t=0$ (Figure 6). The upper bound of each color band in the figure represents the fraction of water in storage that is younger than the oldest water from the storm indicated. The lower bound of the same color band represents the fraction of water in storage that is younger than the oldest water from the next storm, and so on.

The influence of biofilter hydrology on the age structure of stored water (and by implication the age structure of water leaving the biofilter by gravitational drainage under uniform sampling) is striking. During the Filling Phase of each storm (e.g., Storm #3 in Figure 6) new water entering the biofilter from the ponding zone rapidly dominates the age distribution of water in storage for two reasons: (1) the new water fills up portions of storage that were previously dry; and (2) the new water displaces older water, driving it out of the biofilter as gravitational drainage. The first mechanism explains why different storms initially dominate storage to different degrees. For example, the assumed volume of original water in storage at time $t=0$ was relatively small in these simulations ($S_0=0.092$ m, corresponding to the biofilter's field capacity) which explains why Storm #1 very quickly constituted more than 80% of the biofilter's storage (orange band in Figure 6). Because the initial moisture content for the first storm event was set equal to the soil media's field capacity, this last example may be more representative of the situation, during long antecedent dry periods, where biofilters are irrigated only to the extent necessary to maintain soil moisture at field capacity (Ambrose & Winfrey, 2015).

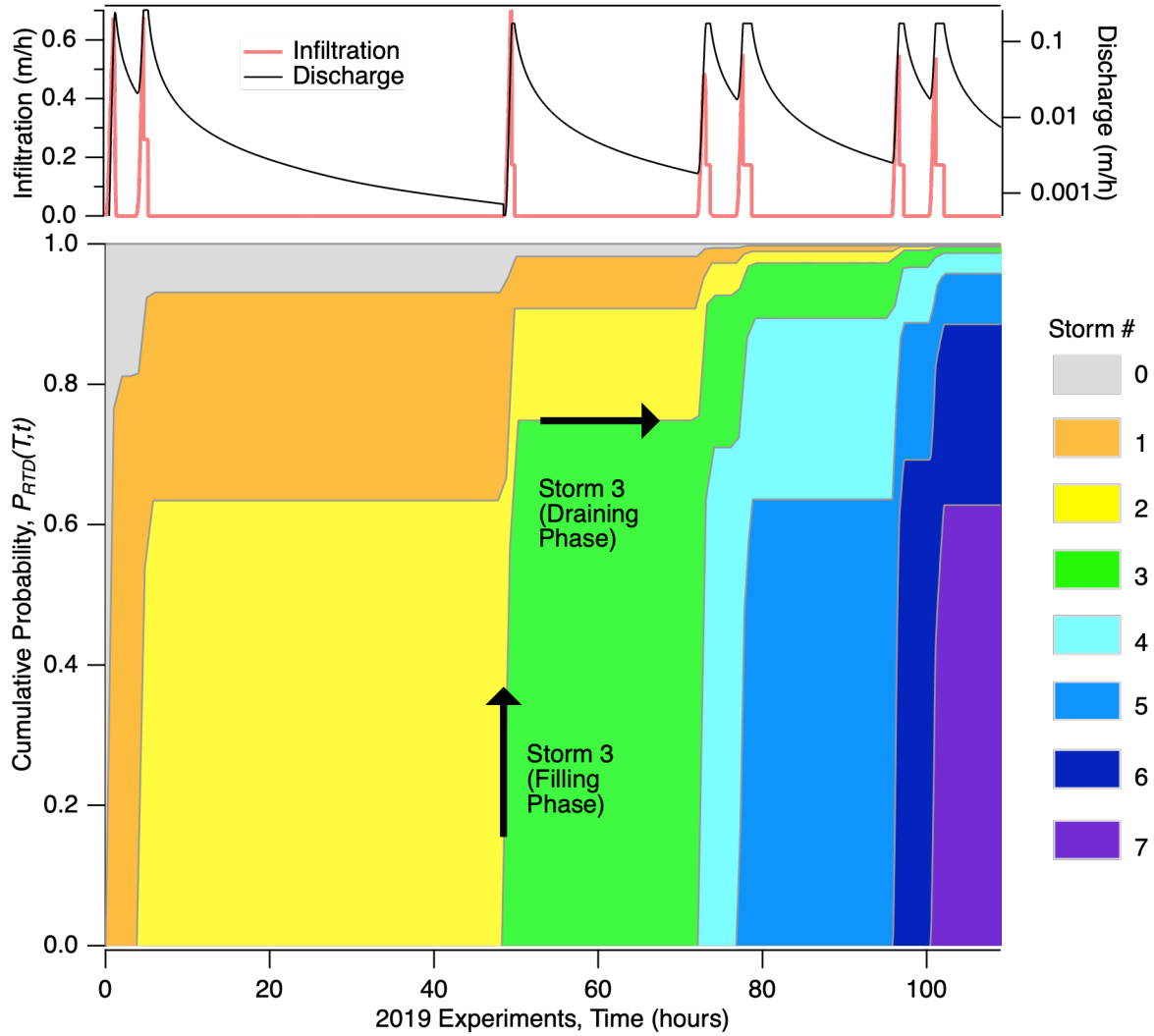


Figure 6. The contribution of original water (Storm #0) and seven experimental storms in 2019 (Storms #1-7) to water storage in the OCPW biofilter over time. Each new storm rapidly occupies at least 50% of storage volume during the Filling Phase. These simulations were carried out using the inferred value for maximum storage of $S_{\max} = 0.42$ m. Top panel indicates infiltration (red curve) and discharge (black curve) for the 2019 storm sequence.

Under a uniform SAS, all water parcels (regardless of their age) have an equal probability of being selected for outflow by gravitational discharge or ET. This explains why, during the Draining Phase, the age structure of water in storage does not change (i.e., during this phase all boundaries in Figure 6 are horizontal lines). Figure 6 also vividly illustrates the two key

attributes of biofilter storage discussed previously: at any time about >50% of water in storage is from the most recent storm while the rest is a mixture of penultimate and earlier storms.

5.3 Age Structure and Water Quality

The age structure of water in storage has significant implications for the treatment credit attributable to, and the pollution exported by, GSI. For example, during the 2019 storm sequence we included a “worst case” scenario (from a water quality perspective) by making one of the experimental storm events, Storm #3, a 50:50 mixture of stormwater and raw sewage. From the thickness of the horizontal portions of the green band in Figure 6 (divided by two to account for the storm’s 50:50 sewage:stormwater mixture) we can infer that the fraction of water in storage that is raw sewage declined over time as follows: 35% (Storm #3), 11% (Storm #4), 4% (Storm #5), 1.2% (Storm #6), and 0.5% (Storm #7). Raw sewage harbors very high concentrations of human fecal bacteria (e.g., in the range of 10^6 *E. coli* mL⁻¹ (Garcia-Aljaro et al., 2018)). Therefore, even after the biofilter has been flushed with four sewage-free storms, the *E. coli* concentration in gravitational drainage could still be as high as 5000 mL⁻¹—more than enough bacteria to close beaches if the biofilter drained to a recreational lake or river (US EPA, 2018)). This example assumes that bacteria behave conservatively which is rarely the case (Lee et al., 2006; Chandrasena et al., 2014b). Indeed, the tendency of biofilters to retain older water might enhance their treatment performance, for example by increasing the opportunity for bacterial removal in the rhizosphere by die-off, grazing by predacious protozoa, and other processes (Chandrasena et al., 2017; Surbeck et al., 2010).

More generally, the retention and release of older water could impact the quality of water released from these systems either positively or negatively, depending on inter-storm pollutant transformation mechanisms. For example, between storms the biofilter media’s organic material

can be respired by resident bacteria, potentially leading to the liberation of ammonium (by ammonification) and nitrate (by nitrification) (Canfield et al., 2010). Thus, water retained in the biofilter from penultimate and older storms could serve as a perpetual source of nitrate that is exported during storm events—a pattern often observed in practice (e.g., Hatt et al., 2009; McPhillips et al., 2018). On the other hand, if anaerobic conditions develop between storms (as is likely to occur if the biofilter contains a submerged zone (Kim et al., 2003)) nitrate may be further transformed to harmless N_2 gas and, potentially, the potent greenhouse gas N_2O (McPhillips et al., 2018) by denitrification.

Evaporative concentration is another aging process that could have potentially significant water quality implications. In northern climates, GSI can serve as a conduit through which deicing salts from road runoff are transferred into shallow groundwater and surface waters, thereby contributing to inland freshwater salinization (Snodgrass et al., 2017). Depending on the degree to which vegetation in these systems fractionate salt during transpiration, evaporative concentration of older water in storage could increase the salinity of water released from GSI, making an already serious problem worse.

5.4 Limitations of the Uniform Selection Function

A key assumption of the TTD model derived and tested in this study is that all water in storage is randomly selected for outflow regardless of its age; i.e., a uniform SAS function was adopted. A primary benefit of this approach is that the resulting age conservation equation is linear and can be solved exactly in the Laplace domain (see Text S4), leading to explicit formulae for the age distribution of water leaving the system by gravitational drainage and the breakthrough concentration of a conservative solute (equations (7a) and (8b), respectively). A potential disadvantage of this approach is that the physical processes by which water and solute are

selected for outflow may not be consistent with the choice of a uniform selection function; i.e., by adopting the uniform SAS function, we may be misrepresenting the underlying physics of water and solute transport through the biofilter.

On the one hand, our model closely reproduces measured bromide breakthrough curves with only a single fitting parameter—the effective maximum storage. On the other hand, inferred values for this parameter declined over the two sets of experiments conducted here, from 0.73 m in 2018 to 0.42 m in 2019. These maximum storage volumes are two to three times the actual storage volume of the biofilter (0.25 m), consistent with the idea that some of the water exfiltrating from our test cell may have found its way back to the outflow tank, either by recirculating through our test cell or by flowing directly to the collection manifold and, from there, to the outflow tank. We can point to several changes in the experimental system that occurred over the two years (e.g., the “leak” was partially sealed and the biofilter was replanted) but these changes might have altered the effective volume of the biofilter, the way in which stored water in the biofilter was sampled for outflow, or both. In particular, we cannot rule out the possibility that the apparent decrease in the maximum effective volume from 2018 to 2019 is an artifact of assuming a uniform SAS function for both years. This equifinality problem underscores a key research priority going forward: to delineate under what conditions the uniform SAS function is appropriate for modeling the transport and transformation of solutes within GSI. While the analytical results presented in this study are valid only for a uniform SAS function, software tools are available for numerically integrating the age conservation equation under non-uniform storage selection as well (e.g., Benettin & Bertuzzo, 2018).”

6. Conclusions

Unsteady TTD theory directly links the hydrology and treatment performance of GSI. Its practical application therefore requires, as a first step, delineation of the unsteady water balance over the GSI element of interest. In this paper we demonstrate that this first step can be accomplished with a simple bucket model that tracks time varying infiltration, storage, ET and gravitational discharge over a control volume drawn around the biofilter soil media, which in our case was lined with an underdrain open to the atmosphere. A set of expressions was proposed and tested for the storage-dependence of water fluxes across the control volume surface, including: (1) an empirical relationship for infiltration that toggles between the inflow of stormwater (when the biofilter media is partially unsaturated) and the saturated hydraulic conductivity (when the biofilter media approaches full saturation); (2) cPET for ET; (3) Kirchner's power-law model for gravitational discharge (equation (3b)); and (4) a simple flow routing scheme that directs a constant fraction, α , of the gravitational discharge to the underdrain and, from there, to the outflow tank.

Generalizing the hydrologic bucket model beyond the experimental system described here may require modifying one or more of these four relationships, for example by adopting a process-based model (such as the Green-Ampt equation (Green & Ampt, 1911)) for infiltration, accounting for the reduction of ET that occurs as moisture content falls below the incipient water stress (Hess et al., 2019; Zhao et al., 2013), tailoring Kirchner's gravitational outflow expression (equation (3b)) by adjusting the minimum and maximum storage values ($S_{\min}$ and $S_{\max}$), and directly measuring, modeling or controlling water loss to the surrounding media (thus eliminating the need for a flow routing scheme).

In our implementation of Kirchner's gravitational outflow model we set the minimum storage value to zero, $S_{\min}=0$, for two reasons: (1) our biofilter was never dry enough to warrant the specification of a value for this parameter; and (2) the very large power-law exponent inferred for Kirchner's gravitational discharge expression ($g = 5$, equation (3b)) ensures that gravitational drainage will be near zero once storage falls below the field capacity of the biofilter media. On the other hand, depending on context, the minimum storage can be equated to: (1) the biofilter media's area-normalized field capacity (e.g., in settings with long antecedent dry periods where even a small gravitational discharge at low storage might lead to water balance errors (Ambrose & Winfrey, 2015)); and (2) the area-normalized volume of the submerged zone for biofilters that include this engineered feature (Kim et al., 2003; Brown & Hunt, 2011).

In the context of our TTD theory, the maximum storage parameter, $S_{\max}$, represents the area-normalized void volume of soil media through which solute and water circulate before being transferred to the next hydrologic response unit; e.g., shallow groundwater in the case of an unlined biofilter or an MS4 drainage network in the case of a lined biofilter (Grant et al., 2013). Our study suggests that this maximum storage may exceed the biofilter's physical void volume, due to lateral exfiltration of water and solutes into the surrounding soil. Roughly speaking, from the results presented here, it appears that a volume loss of around 55% (close to the design goal for GSI of 67% (Davis, 2008)) increases the effective maximum storage volume by a factor of two to three.

With the unsteady water balance in hand, we next solved the age conservation equation under the assumption that stored water is randomly selected for outflow regardless of its age (i.e., we adopted the uniform SAS function). From this solution explicit expressions were derived for the mean age of water in storage (and leaving the biofilter as ET and gravitational

discharge), various age percentiles, as well as the breakthrough concentration of a conservative solute (equations (8b) and (9b)). When compared to bromide breakthrough data measured during our field experiments, we find the model over samples young water, either because the uniform SAS function oversamples young water in storage, or because there is simply not enough old water in storage to sample from (Benettin et al., 2013; Harman, 2015).

Given the magnitude of lateral exfiltration in our system, it is unlikely that water entering the outflow tank was selected exclusively from water stored within the physical boundaries of the biofilter test cell. Indeed, when we allow the maximum storage volume of the biofilter to be a free variable, the inferred volumes are 70% to 196% larger than the biofilter's void volume, consistent with the hypothesis that exfiltration increases the effective storage experienced by solutes as they transit through the system. The concordance between predicted and measured bromide breakthrough concentrations improves dramatically after taking this extra storage into account (Figures 4b and 4d). Remarkably, the final model—which includes both the unsteady water balance over the biofilter media (equation (1a)) and the convolution integral for solute breakthrough (equation (9b))—has only one fitting parameter: the effective volume of the biofilter.

Looking forward, TTD theory could inform the design of GSI elements, for example by allowing engineers to tailor passive features of the porous media component of these systems—such as their depth, porosity and saturated hydraulic conductivity—to achieve target mixtures of young and old water in storage and outflow. Opportunities also exist to control water quality “on the fly,” for example by embedding TTD theory into control algorithms that dynamically actuate inflows and outflows using so-called smart stormwater technology (Kerkez et al., 2016). The parsimony, extensibility and predictive power of TTD theory opens up new possibilities for

modeling and optimizing pollutant removal at the scale of individual biofilters, as well as GSI networks and the urban catchments in which they are embedded (Hrachowitz et al., 2016).

Table 1. Table of variables with their definition and units, roughly in order of appearance.

Variable	Definition	Units
<i>Hydrologic Variables</i>		
t	Time	T
$S(t)$	Area-normalized volume of water in storage in the biofilter	L
$I(t)$	Area-normalized infiltration rate of water into the biofilter from the ponding zone	$L\ T^{-1}$
$Q(t)$	Area-normalized gravitational discharge of water out of the biofilter	$L\ T^{-1}$
$ET(t)$	Area-normalized evapotranspiration across the top boundary of the biofilter	$L\ T^{-1}$
S_0	Area-normalized volume of water in storage at time $t=0$	L
$I(t)$	Area-normalized inflow of stormwater to the ponding zone of the biofilter	$L\ T^{-1}$
K_{sat}	Average saturated hydraulic conductivity of biofilter media	$L\ T^{-1}$
S_{max}	Area-normalized maximum water storage of the biofilter	L
a, b	Empirical constants for the power-law stream flow recession model	-
S_{min}	Area-normalized residual storage at which all gravitational discharge ceases	L
g	Power law exponent relating gravitational discharge and storage	-
d_b	Depth of biofilter media	L
θ_s	Porosity of biofilter media	-
θ_r	Residual soil water content	-
l	Tortuosity parameter	-
α_{vg}, n_{vg}	Van Genuchten shape parameters	L, -
α	Fraction of gravitational discharge that is routed to the biofilter underdrain	-
s_0	Initial biofilter moisture content	-
<i>Transit Time Distribution Variables</i>		
T	Water age	T
$S_T(T, t)$	Age-ranked storage equal to area-normalized volume of water stored in the biofilter media at any time t with ages T or younger	L
$P_{RTD}(T, t)$	CDF for the fraction of stored water with ages less than or equal to T at time t (the unsteady RTD of water in storage)	-
T_0	The age of water in storage at time $t=0$	T

$H(\bullet)$	Heaviside function	-
$\bar{p}_q(T,t)$	CDF for the fraction of water exiting the biofilter as gravitational discharge with ages T or younger at time t (backward TTD)	-
$\bar{p}_{ET}(T,t)$	CDF for the fraction of water exiting the biofilter as evapotranspiration with ages T or younger at time t (backward TTD)	-
$\Omega(S_T,t)$	Ranked StorAge Selection function	-
$\Omega_q(S_T,t)$	Ranked StorAge Selection function for gravitational discharge	-
$\Omega_{ET}(S_T,t)$	Ranked StorAge Selection function for evapotranspiration	-
$S_T^u(T,t)$	Age-ranked storage under uniform selection	L
$\delta(T)$	Dirac delta function	T ⁻¹
$p_{RTD}^u(T,t)$	CDF for the fraction of stored water with ages less than or equal to T at time t under uniform selection	-
$p_{RTD}^u(T,t)$	PDF for the fraction of stored water with age T at time t under uniform selection	T ⁻¹
$\bar{p}_q^u(T,t)$	PDF for the fraction of water exiting biofilter as gravitational discharge with age T at time t under uniform selection (backward TTD)	T ⁻¹
$\bar{p}_{ET}^u(T,t)$	PDF for the fraction of water exiting biofilter as evapotranspiration with age T at time t under uniform selection (backward TTD)	T ⁻¹
$\mu_{RTD}^u(t)$	Mean age of water in storage under uniform selection	T
$C_q(t)$	Concentration of solute in water leaving the biofilter by gravitational drainage	M L ⁻³
$C_f(t_i,T)$	Concentration of solute in water that entered the biofilter at time t_i and exited the biofilter as gravitational discharge with age T	M L ⁻³
t_i	Time water and solutes infiltrated into the biofilter across its upper boundary	T
C_0	Concentration of solute present in water stored in the biofilter at time $t = 0$	M L ⁻³
$C_{J,m}$	Concentration of solute in the inflow of the m -th storm	M L ⁻³
$t_{m,s}$	Start time of the m -th storm's inflow	T
$t_{m,e}$	End time of the m -th storm's inflow	T
$f_n(t)$	Fraction of water in storage that is associated with the n -th storm	-

Chapter 4

Can Smart Stormwater Systems Outsmart the Weather? The Limits of Stormwater Real-Time Control for Delivering Human and Environmental Benefits in Southern California

1. Introduction

Many water-stressed regions, such as Southern California, have historically relied on a combination of imported water and unsustainable use of local ground and surface waters (consuming freshwater faster than it is replenished) (Luthy et al., 2020; Pincetl et al., 2019). Thus, decision makers in the region are increasingly looking for more resilient and sustainable water supply solutions as they grapple with two major stressors: continued population growth and increased precipitation volatility resulting from climate change (Grant et al., 2012; Grant et al., 2013; Low et al., 2015; Gleick 2018; Swain et al., 2018). For example, the University of California, Los Angeles-led Sustainable Los Angeles Grand Challenge aims to transition Los Angeles County to 100 percent local water by 2050, and stormwater capture is poised to play an important role in meeting this goal (Federico et al., 2019). At the state level, the California State Water Resources Control Board set a goal of increasing California's stormwater use, relative to 2007 levels, by > 1 million acre-feet per year by 2030 (CA State Water Board, 2016). In urban settings, increased stormwater capture also reduces the environmental toll from storm drain systems, also known as municipal separate storm sewer systems (MS4s) (Walsh et al., 2005; Askarizadeh et al., 2015). MS4s discharge high velocity and untreated stormwater runoff (often carrying high pollutant loads) to receiving waters, causing hydromodification of streams, surface

water impairments, beach closures, and cascading ecological impacts (National Academies, 2009; US EPA, 1983; Ahn et al., 2005; Grebel et al., 2013; Reeves et al., 2004; Walsh et al., 2005).

One major obstacle to increasing stormwater capture in Mediterranean climates, such as Southern California, is that most precipitation occurs during large storm events in the winter and spring when outdoor water demand is low, while the summer and fall months are typically dry when outdoor water demand is high (Grant et al., 2020). As a result, the capacity to store stormwater is a limiting factor, which Southern California has largely addressed by relying on subsurface storage in shallow aquifers (Luthy et al., 2020). Smart stormwater systems may also help. These systems rely on an integrated network of sensors and control structures for real-time control (RTC) of stormwater infrastructure at a systems level (Bartos et al., 2018; Kerkez et al., 2016). For example, smart stormwater detention ponds respond to weather forecasts by releasing stored water in advance of precipitation events (Carpenter et al., 2014; Gaborit et al., 2013; Gaborit et al., 2016). Smart systems have the potential to address many of the challenges faced by urban stormwater managers, including detecting and reducing combined sewer overflows (CSOs) (US EPA 2018; Hofer et al., 2018; Lund et al., 2018; Campisano et al., 2016) and forecasting and reducing urban flood risk (Eggiman et al., 2017; Jacopin et al., 2001; Garofalo et al., 2017). Recent studies have explored the use of RTC technology for managing environmental flows (Horne et al., 2018) and shaping streamflow (Mullapudi et al., 2018), as well as multi-objective scenarios that optimize stormwater retention and pollutant removal (Muschalla et al., 2014; Mullapudi et al., 2017; Gaborit et al., 2013), reduce flooding and maximize stormwater harvesting (Han et al., 2011; Behzadian et al., 2018), and combine retention, water supply, and stream baseflow benefits (Xu et al., 2018). RTC technology allows for stormwater systems that

are dynamic and adaptable in the face of uncertainty surrounding future land use changes, population growth, and climate change (Hill et al., 2014; Kerkez et al., 2016; Xu et al., 2021). Given the increasing importance of stormwater as a freshwater resource, RTC can play a large role in future stormwater capture systems, although it is unclear to what extent RTC systems can address the primary challenge of unevenly distributed precipitation in water scarce areas like Southern California.

In the search for water supply solutions, universities can serve as living laboratories for new ideas that require field-testing before they are implemented on a city- or state-wide scale (Pierce et al., 2021a). In that spirit, the five University of California campuses located in Southern California participated in a multi-year research project, “Fighting Drought with Stormwater,” focused on identifying and overcoming perceptual, regulatory, and technical barriers associated with making stormwater a significant component of Southern California’s water supply portfolio (Pierce et al., 2021b; Parker et al., 2021). Focusing on the University of California, Irvine (UCI) campus in Irvine, CA, as a test bed, this paper sets out to answer the following question: *what are the “best-case” limits of stormwater RTC for delivering both water supply and environmental benefits in Southern California, and how do these benefits depend on the cumulative annual volume and seasonality of precipitation?* To answer this question we estimate stormwater runoff volumes generated from the UCI campus using a stochastic hydrologic model and determine the associated water supply and environmental benefits for a stormwater capture system, with and without RTC. Specifically, we set out to test the following three hypotheses: (H1) an RTC-enhanced, or “smart,” stormwater storage system yields greater human water supply benefits, measured as the percent of human water demand satisfied, than a non-RTC system; (H2) a smart stormwater storage system yields greater environmental benefits,

measured as the percent of stormwater runoff captured, than a non-RTC system; and (H3) the level of human and environmental benefits provided by RTC is dependent on cumulative annual rainfall and rainfall evenness.

Our study is noteworthy in several respects. First, we rely on copulas to derive probability distributions for the human and environmental benefits achieved by a stormwater capture RTC system under various scenarios of annual cumulative rainfall (dry, average, or wet years), rainfall evenness, and choice of RTC algorithm. The resulting probability distributions provide an intuitive and straightforward approach for testing the three hypotheses outlined above, and could serve as the starting point for the development of novel financial instruments, such as environmental impact bonds, to fund the construction and operation of stormwater RTC systems in practice (Brand et al., 2020; Hererra et al., 2019). Second, using our hydrological analysis of stormwater capture on the UCI campus as a test case, we explore the importance of context-specific knowledge and community engagement in determining what makes an RTC-enhanced stormwater capture system “smart.”

2. Methods

2.1 Campus Runoff Model

UCI is located adjacent to San Diego Creek, an urban waterway that drains to an ecologically important tidal saltwater wetland (Upper Newport Bay) and from there to the coastal ocean through a popular marina (Lower Newport Bay) (Figure 1a, 1b). UCI’s main campus contains several stormwater sub-drainages; all stormwater from the largest sub-drainage (area of $\sim 2 \text{ km}^2$) is routed without treatment directly to San Diego Creek through a single stormwater culvert (Figure 1c, 1d). To estimate the volume of runoff generated by this sub-drainage, we used a

stochastic hydrologic framework implemented in MATLAB (MathWorks, Natick, MA) and Hydrus 1D (PC-Progress, Prague, Czech Republic). The model produces stochastic realizations of daily runoff from the UCI campus over 27 years, taking as input historical daily measurements (from 1990 to 2016) of local precipitation (NOAA NCEI) (precipitation scenario P-1; Figure 2a), irrigation (determined from UCI's recycled water consumption, as UCI relies almost exclusively on recycled water for irrigation (UC Irvine, 2017)) and evapotranspiration (Harris et al., 2014). Runoff was estimated from both the pervious area (47% of the total area; using Hydrus 1D) and impervious area (53% of the total area; using the rational method (Brooks et al. 2013) assuming a unit runoff coefficient) of the sub-drainage. To account for hydrologic variability, the Hydrus 1D model randomly draws from probability distributions of soil texture and depth to shallow groundwater (further details in Text S1, Supporting Information (SI), Appendix C). For each precipitation event in the time series, the magnitude of the precipitation was perturbed by a multiplier randomly drawn from a uniform distribution (ranging from 0.8 to 1.2). By repeating the 27-year modeling exercise ten times, this approach yielded nearly 100,000 stochastic realizations of daily runoff volume from the sub-drainage. To isolate the effect of rainfall evenness, we re-ran the runoff calculations described above using a counterfactual precipitation scenario (P-2; Figure 2a), created by scaling a 26-year daily timeseries (1990-2016, excluding snowfall) of precipitation for Washington, DC (which historically receives rainfall more evenly distributed throughout the year compared to Southern California) (NOAA NCEI) to have precisely the same average annual rainfall as the Southern California rainfall scenario P-1. By investigating the best-case limits of stormwater RTC at UCI for both P-1 and P-2 scenarios, we were able to isolate the influence of Southern California's semi-arid Mediterranean climate

(specifically, its evenness, see Section 2.2), all else held equal, on the environmental and human benefits of a smart stormwater collection system.

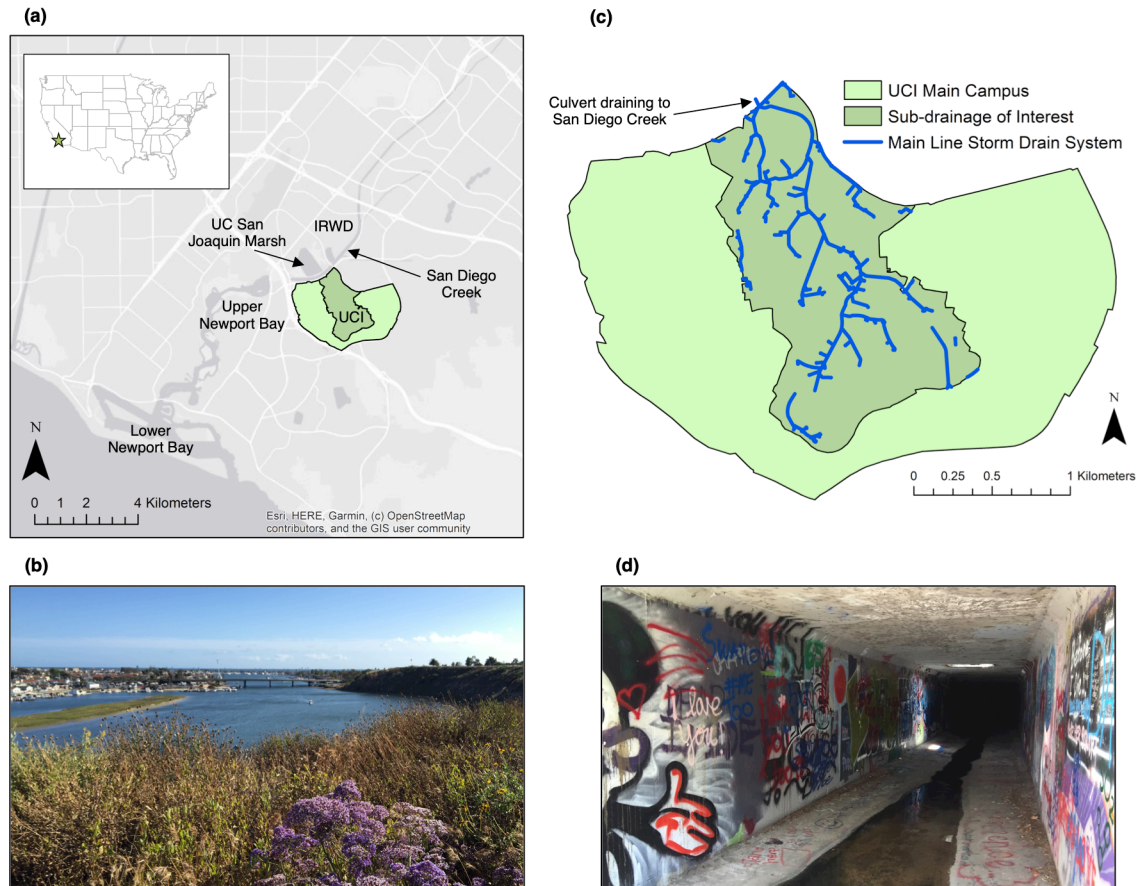


Figure 1. (a) The UC Irvine campus (green shaded area) is located close to the UC San Joaquin Marsh, the Irvine Ranch Water District (IRWD) natural treatment system and water recycling facility, and San Diego Creek. (b) San Diego Creek flows into Upper Newport Bay and then Lower Newport Bay, transitioning from natural wetland habitat to a popular recreational marina. (c) The largest campus stormwater sub-drainage (darker green shaded area) routes all stormwater runoff from the sub-drainage through a culvert (shown in (d)) to San Diego Creek.

2.2 Gini Index

We adopted the Gini index as a measure of rainfall evenness where y_i is the daily precipitation sorted in increasing order, and n is the number of days per year (365 or 366) (Rajah et al., 2014):

$$G = \frac{1}{n} \left(n+1 - 2 \left(\frac{\sum_{i=1}^n (n+1-i) y_i}{\sum_{i=1}^n y_i} \right) \right) \quad (1)$$

The Gini index ranges between 0 and 1, where $G=0$ corresponds to the limit where annual rainfall is evenly distributed across 365 days and $G=1$ corresponds to the limit where all annual rainfall occurs on a single day (Rajah et al., 2014).

2.3 Tank Simulations

We modeled the performance of a hypothetical stormwater runoff storage system, or “tank,” that intercepts and captures stormwater runoff from the culvert before it reaches San Diego Creek, with or without RTC. Based on preliminary simulations with tank sizes ranging from 1,000 to 60,000 m³ we found that the environmental and human benefits (as described below) saturated for tanks larger than 10,000 m³ (see Figure S1, SI); we therefore set the tank size to 10,000 m³, consistent with our goal of assessing the theoretical upper limit of what is achievable with RTC technology. The siting and construction of a tank this size would cost on the order of \$10-20M USD (City of Alexandria, VA, 2015)), and is therefore at the outer limits of what is financially feasible for many communities, including university campuses. To assess the human benefits of the tank, we used a general demand profile for the captured stormwater (expressed as a daily time series) that alternates between six months of low demand in the winter (November-April, 250 m³/day, 5% of the daily volume of wastewater generated at UCI) and six months of high

demand in the summer (May through October, 500 m³/day, 10% of the daily volume of wastewater generated at UCI) (UC Irvine, 2017) (Figure 2a). These summer and winter demand profiles were derived from discussions with local university, environmental, and utility stakeholders.

Water balance calculations were carried out on a daily time step as follows. The volume of water in the tank was updated each day by adding the current day's incoming runoff (generated by the campus runoff model, see previous section) to the tank's stored runoff volume from the previous day, after subtracting the amount of stormwater used to satisfy daily demand. On days where the volume of runoff from the sub-drainage exceeded tank capacity, excess runoff was diverted to San Diego Creek, thereby reducing the environmental benefit conferred. Conversely, on days when the tank was empty, demand was not met, thereby reducing the human benefit conferred. This water balance was performed for the two precipitation scenarios (P-1 and P-2) described above and three RTC scenarios as follows: (1) a passive control tank that has no knowledge of future weather conditions (Passive); (2) an RTC-enhanced tank that has perfect knowledge of the runoff volume that will occur one day in advance (RTC-1); and (3) an RTC-enhanced tank that has perfect knowledge of the runoff volume that will occur two days in advance (RTC-2) (Figure 2b). Based on this perfect knowledge of future weather conditions, the RTC algorithm released additional volume to San Diego Creek, equal to the runoff volume slated to occur in the next one or two days, up to a maximum of 5000 m³ per day (Figure 2b). For each scenario, tank performance was quantified based on the fraction of annual stormwater runoff volume captured (*environmental benefit* of reducing stormwater runoff flows to San Diego Creek) and the fraction of annual demand satisfied (*human benefit* of augmenting local water supply).

2.4 Copula Based Bivariate Distributions and Conditional Probabilities

To quantify how annual rainfall and rainfall evenness affects the human and environmental benefits achieved by the three RTC scenarios described above (no knowledge of future rainfall, one day foreknowledge, and two days foreknowledge), we prepared marginal probability distributions of annual rainfall, percent of annual runoff volume captured (environmental benefit), and percent of annual demand satisfied (human benefit) from the approximately 100,000 daily runoff and tank water balance simulations as described in Sections 2.1 and 2.3. Because the human and environmental benefits of the tank are measured as percentages, their marginal distributions were bounded on the support 0 and 100%. Marginal distributions for annual rainfall and the human or environmental benefit conferred by the stormwater capture tank were joined by a copula to yield bivariate cumulative distribution functions (CDFs) of the form $F_{BR}(b, r) = C[F_B(b), F_R(r)]$. Here, B and R are random variables for the annual benefits achieved (fraction of either runoff captured or demand satisfied) and annual rainfall, respectively, b and r are specific realizations of these random variables, and C is the CDF of the copula. We used the Multivariate Copula Analysis Toolbox (MvCAT, Sadegh et al., 2017) to select appropriate copula functions from the Archimedean, Plackett, and Burr families (based on Bayesian Information Criterion (BIC) ranking) and infer distribution parameters from our annual rainfall and human or environmental benefits timeseries. The probability density function (PDF) form of the human or environmental benefits, conditioned on a specific annual rainfall, was then calculated as follows (Madadgar et al., 2017).

$$f_{B|R}(b|r) = c[F_B(b), F_R(r)]f_B(b) \quad (2)$$

Here, c is the PDF form of the copula and the function $f_B(b)$ is the PDF of the marginal distribution for annual benefits conferred by the tank. Specific conditioning events considered included dry (5th percentile), average, or wet (95th percentile) years (annual rainfall of 6, 23, and 52 cm, respectively for P-1; 18, 23, and 30 cm, respectively for P-2). The copula analysis was numerically implemented in the computational software package Wolfram Mathematica (Wolfram, Champaign, IL, version 10.1).

3. Results and Discussion

3.1 Rainfall and Runoff

The two rainfall scenarios (P-1 and P-2) examined here have the same average annual precipitation (23 cm), but P-1 reflects the strongly seasonal rainfall pattern in Southern California (annual average Gini index of 0.96) while P-2 is a counterfactual scenario in which the same annual average rainfall is more evenly distributed over the year (annual average Gini index of 0.87) (Figure 2a). By virtue of the way the counterfactual scenario was constructed (by scaling rainfall timeseries measured in Washington D.C., see Methods), the distribution of cumulative annual rainfall for scenario P-2 is relatively narrow, ranging from roughly 20 to 40 cm (blue probability distribution in Figure 2c). Rainfall in Southern California, on the other hand, varies considerably from year-to-year, resulting in a broad distribution of cumulative annual rainfall for scenario P-1, from less than 10 cm to nearly 60 cm during dry and wet years, respectively (grey probability distribution, Figure 2c). Not surprisingly, the runoff generated from these two scenarios exhibit similar patterns, with relatively broad and narrow ranges of annual runoff, respectively, under scenarios P-1 (0.3 to $>5 \times 10^5 \text{ m}^3$) and P-2 (0.5 to $1.5 \times 10^5 \text{ m}^3$).

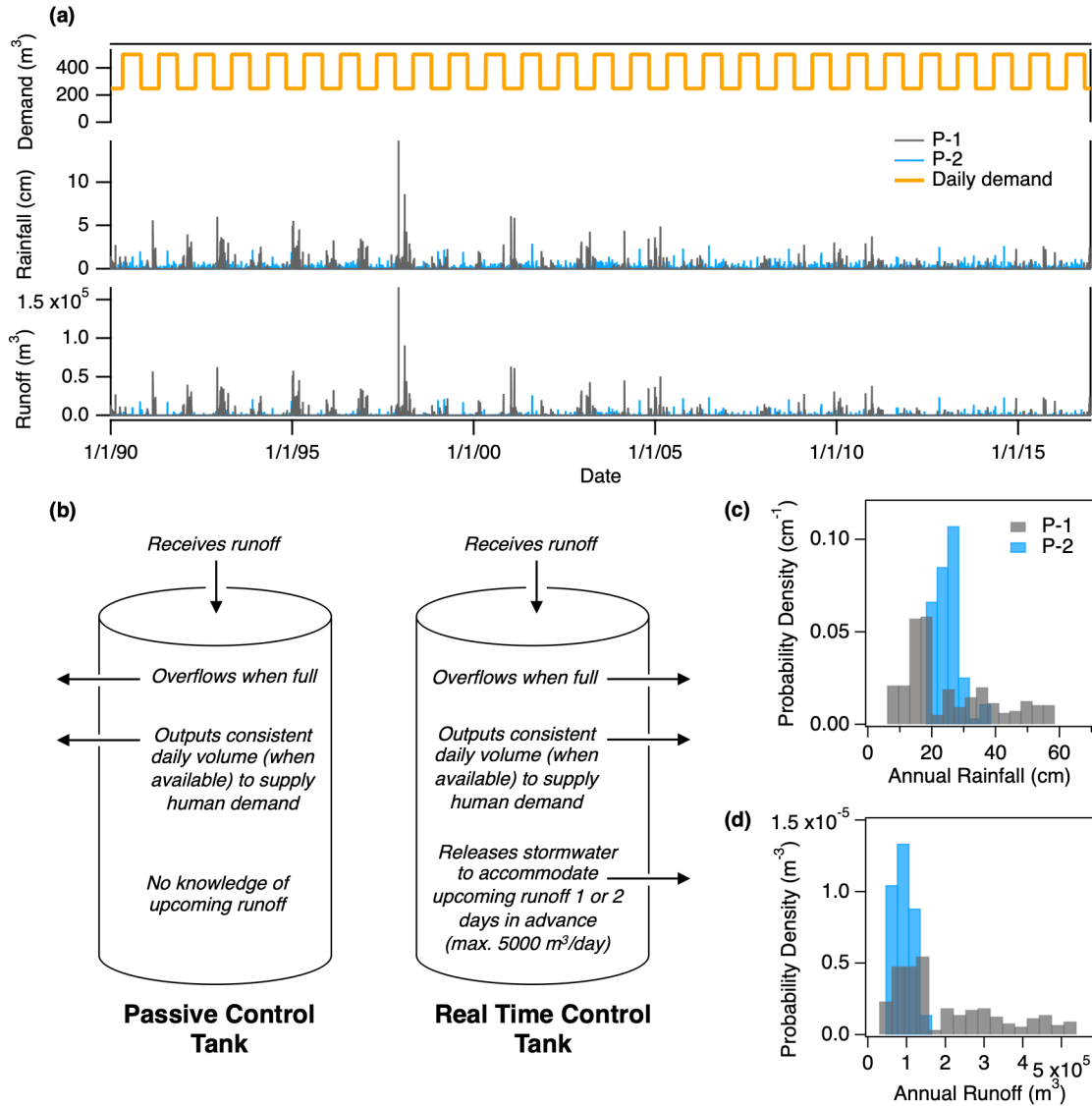


Figure 2. (a) Time series of daily water demand, rainfall, and simulated runoff generated by the largest UCI stormwater sub-drainage over 27 years for two precipitation scenarios (P-1, less evenly distributed rainfall, and P-2, more evenly distributed rainfall). (b) Schematic showing the key features of passive and real time control stormwater storage tanks described in this study. (c) Distribution of annual rainfall and (d) runoff for P-1 and P-2 precipitation scenarios.

While P-1 and P-2 have the same average annual rainfall, the average annual runoff generated from P-1 ($1.9 \pm 1.3 \times 10^5 \text{ m}^3$) exceeds that for P-2 ($7.4 \pm 2.5 \times 10^4 \text{ m}^3$), (Figure 2d). Under the P-1 scenario, most of the annual rainfall occurs in a small number of large storm events in the winter. These large storms rapidly saturate the soil in pervious areas of the UCI catchment resulting in

relatively large runoff events. Under the counterfactual P-2 scenario, rain events are generally smaller and distributed throughout the year. As a result, the soil in permeable areas is less frequently saturated and runoff events are less frequent and smaller in size.

3.2 Copula-Based Conditional Probability Analysis

The copula-based conditional probability analysis reveals that the human benefit conferred by the stormwater capture system (i.e., the percent of annual water demand satisfied by the tank) depends strongly on the volume of rain that falls in a particular year (Figure 3a). Probability distributions of the human benefit conferred by the stormwater capture system shift progressively rightward for dry (5th percentile), average, and wet (95th percentile) years. This rightward shift is evident for both rainfall scenarios (P-1 and P-2) but is especially dramatic for the counterfactual scenario (P-2). During wet years the percent of annual demand satisfied increases from 20 - 60% if the rainfall is uneven (P-1) to 50 - 80% if the rainfall is more evenly distributed (P-2). During dry years the percent of annual demand satisfied increases from 10 - 40% if the rainfall is uneven (P-1) to 20 - 60% if the rainfall is more evenly distributed (P-2). The inclusion of RTC (with one or two days of perfect foreknowledge of future weather) has no effect on the human benefit achieved across all scenarios evaluated (i.e., the probability distributions for the passive, RTC-1 and RTC-2 scenarios all overlap, Figure 3a). This striking result is a consequence of the RTC algorithm we adopted: the algorithm releases water in advance of storms, but a full tank (whether a passive tank that filled up and overflowed, or a smart tank that released water in advance and then filled up) can only supply so much demand before it goes dry during the interval between rain events. RTC systems are often designed to prioritize runoff capture at the expense of water supply, and thus RTC nearly always leads to a reduction in human benefit (because if water is

released prior to a storm it is not later available to satisfy human demand) (Xu et al., 2020). In our simulations we avoided that trade-off by always satisfying the daily demand before discharging any pre-storm release for the day (and hence the introduction of RTC-1 or RTC-2, in our case, had no effect on the probability distributions of human benefit).

Because runoff events are generally smaller under P-2 (see above), the tank is relatively efficient at delivering environmental benefits for this rainfall scenario, with >50% of annual runoff volume captured across all three conditioning events (dry, average, and wet years) and across all three tank configurations (passive, RTC-1, and RTC-2) (Figure 3b, bottom row). RTC provides a modest improvement in the delivery of environmental benefits during average and wet years; e.g., during a wet year, the percent of annual runoff captured increases from >50% for a passive tank, to >70% for either RTC-1 or RTC-2 (bottom right panel, Figure 3b). RTC has the most dramatic impact on the delivery of environmental benefits under the Southern California rainfall scenario (P-1) (top row of panels, Figure 3b). For this scenario and during average and wet years, the distribution of environmental benefits shifts progressively rightward as the tank goes from passive to RTC-1 to RTC-2. The influence of RTC is less evident for P-1 during a dry year (upper left panel, Figure 3b). In this case, the rainfall events are relatively small and infrequent and thus the tank can accommodate all of the runoff generated with or without RTC. Interestingly, the environmental benefits conferred by the tank are most likely to be improved by RTC for the uneven rainfall conditions representative of Southern California rainfall (P-1).

Relative to the set of hypotheses articulated earlier we can conclude the following. Within the context of the scenarios evaluated in this study (more on this later): (*H1*) RTC does not improve the delivery of human water supply benefits; (*H2*) RTC does improve the delivery of environmental benefits, particularly during average and wet years; and (*H3*) the environmental

benefits provided by RTC are strongly influenced by rainfall evenness, with the greatest impact observed for the uneven rainfall scenario (P-1) representative of Southern California.

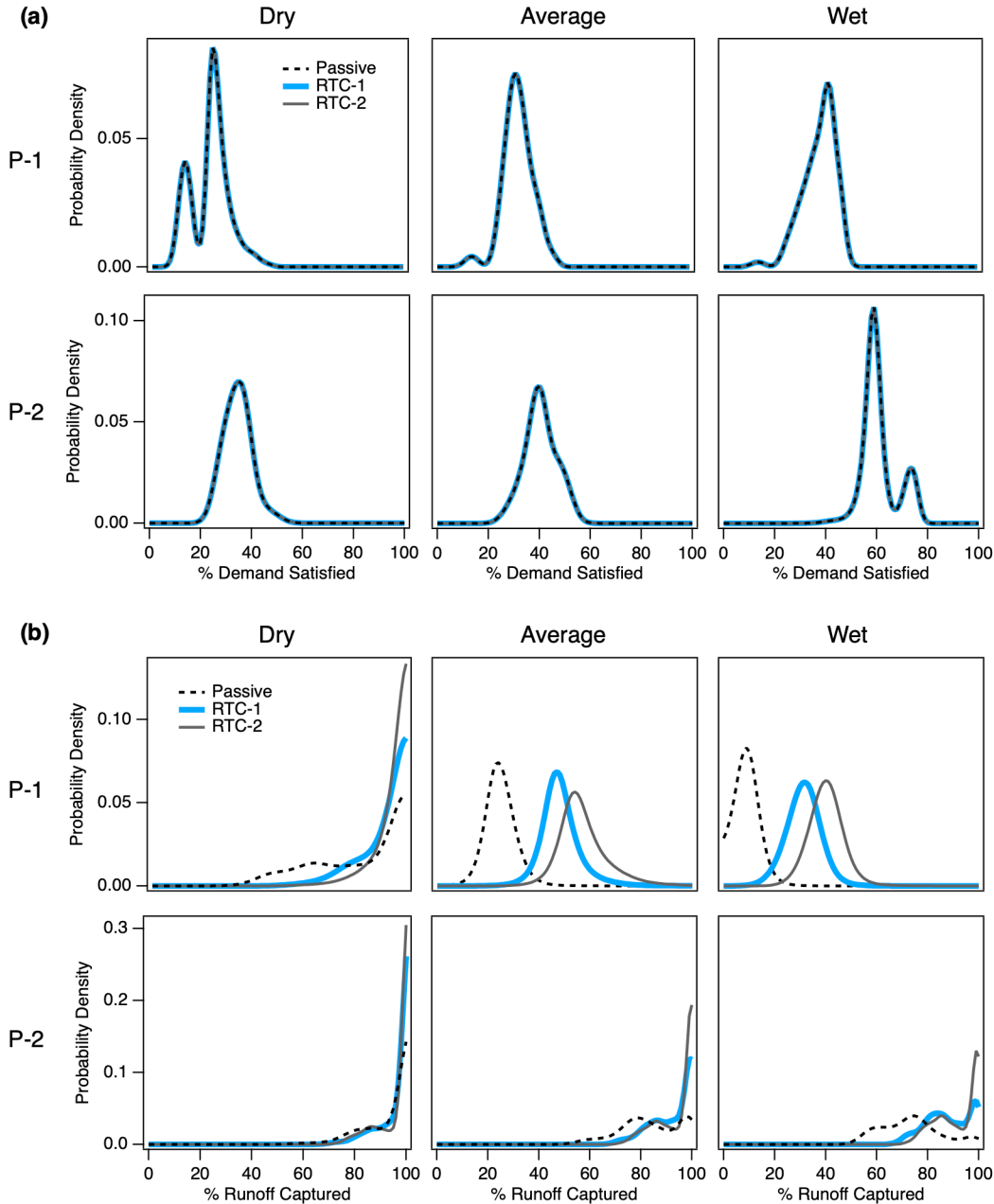


Figure 3. Probability density functions for (a) the percent of water demand satisfied and (b) the percent of runoff captured conditioned on dry (5th percentile), average, or wet (95th percentile) annual rainfall for precipitation scenarios P-1 and P-2. Colored curves represent the performance of a passive tank (dashed black curves), a real-time control tank with one day of weather foreknowledge (blue), and a real-time control tank with two days of weather foreknowledge (gray).

3.3 Informing Cost-Benefit Analysis

The copula-based conditional probability analysis utilized in this study is a straightforward and intuitive approach for identifying the conditions under which RTC of stormwater captures systems can improve the delivery of human or environmental benefits. This approach may also be useful for the development of novel financial instruments for underwriting smart stormwater infrastructure. For example, environmental impact bonds (EIBs) are an emerging funding mechanism for financing watershed interventions such as stormwater capture systems (Brand et al., 2020; Martin, 2017). In this funding framework, investors provide capital for implementing a stormwater system, and are then repaid with interest over time by watershed stakeholders (who benefit from reduced management costs as a result of the intervention) (Balboa, 2016; Brand et al., 2020; Herrera et al., 2019). For the stormwater capture system described in this study, stakeholders would achieve cost savings related to both the human and environmental benefits of the system (e.g., by satisfying some portion of water demand with local stormwater instead of buying water, and by achieving compliance with Clean Water Act regulations, thus avoiding fines or other costly interventions). Because these cost savings are used to pay back investors over time, EIB development requires probability distributions of the likely benefits of investing in stormwater RTC, compared to a passive system—precisely the information provided by our conditional probability distributions. Furthermore, by conditioning distributions of human and environmental benefits on cumulative annual rainfall (as we have done here), investors can quantitatively evaluate the risk associated with investing in RTC technology under different possible climate futures.

3.4 Opportunities to Increase the Benefits of RTC in Southern California

Our study highlights possible shortcomings of RTC for stormwater capture in areas with uneven rainfall, but points to several opportunities for improvement. An increase in the fraction of runoff captured might be achieved by relaxing the constraint, built into our RTC algorithm, that the total daily volume of pre-storm water released to San Diego Creek can never exceed 5000 m³ (Figure 2b). This constraint was imposed to address concerns raised in the literature that RTC will not address hydromodification and ecological impacts of stormwater runoff, if it simply shifts the timing of high flow events from after a storm (without RTC) to before a storm (with RTC) (Xu et al., 2020). Releasing a daily volume of 5000 m³ over 24 hours equates to an increase in stream flow of approximately 0.06 m³s⁻¹, corresponding to 10% of the dry weather base flow (upper limit 0.6 m³s⁻¹) in San Diego Creek (US EPA Region 9, 2002). However, further iterations of this study could include more sophisticated RTC systems that capture and release runoff to San Diego Creek in accordance with specific regional flow targets (Mazor et al., 2018; Mullapudi et al., 2018; Stein et al., 2017).

In addition, increasing the rainfall forecast window may improve the environmental benefits of the system, because RTC systems can better mimic natural streamflow conditions in their release regime by spreading out the pre-storm release over several days (Xu et al., 2020). Spreading out the pre-storm release over several days could also allow for larger overall pre-storm release volumes (without exceeding our 5000 m³ daily cap), thus increasing the capacity for runoff capture. However, our results also indicate that increasing the rainfall forecast window would not improve human demand satisfaction.

The human and environmental benefits of a smart stormwater system might also be improved by careful consideration of the social, political, and environmental context. For

example, discharging water directly to San Diego Creek is a straightforward strategy for pre-storm release, but after further analysis of UCI's surroundings we identified three alternative possibilities; namely, sending the pre-storm water to: 1) the nearby UC San Joaquin Marsh (an important area of wetland habitat in the UC Natural Reserve System), which has an environmental water demand that regularly exceeds its supply, 2) the nearby Irvine Ranch Water District's (IRWD) Michelson Water Recycling Plant for tertiary treatment and subsequent distribution to consumers via IRWD's recycled water system, or 3) IRWD's nearby treatment marsh to undergo natural treatment before it is released to either the UC San Joaquin Marsh or San Diego Creek (Figure 1a). These possible uses of the pre-storm water are also possible endpoints for water demand satisfaction, highlighting the opportunity for synergies between human and environmental benefit endpoints at this particular site. Using the tank to capture dry weather runoff (e.g., from over-irrigation of lawns, car washing activities in the catchment, and so on) could also help satisfy some portion of water demand during the summer.

Embedding campus-scale (or smaller) smart stormwater systems into larger smart stormwater networks could also help overcome some of the limitations of RTC observed in this study. For example, a regionally integrated smart network could rely on distributed tanks and green infrastructure for runoff capture, and then divert the captured runoff to central spreading basins for groundwater recharge (Luthy et al., 2020). Implementing "real-time distributed control" of stormwater could expand both the capacity of the system (thus reducing overflow) and the possibilities for delivering water supply, thus increasing overall reliability and performance (Maiolo et al., 2020; Ramsey et al., 2020; Xu et al., 2021).

3.5 Defining “Smart”

In this study, we defined a smart stormwater system as a storage tank that discharged water in advance of upcoming rainfall, based on perfect knowledge of the weather forecast either one or two days in advance. This approach is consistent with the literature, which has generally focused on stormwater RTC with the primary goal of optimizing environmental benefits (e.g., Gaborit et al., 2013; Kerkez et al., 2016; Muschalla et al., 2014). However, stormwater systems have the potential to be “smart” in many different ways. A biased definition of smart (e.g., researchers prioritizing runoff capture over water supply in the RTC algorithm) can exacerbate inequities that already exist in urban environments (Schell et al., 2020; Taguchi et al., 2020). Broadly, artificial intelligence has the potential to increase inequalities both between and within countries, and can both enable and inhibit the achievement of the United Nations Sustainable Development Goals (Vinuesa et al., 2020). Community engagement should be a crucial part of future smart stormwater implementation to ensure that biases inherent in optimizing infrastructure performance do not erode trust in stormwater systems (Ewing & Demir, 2021; Finewood et al., 2019). Cities implementing smart stormwater systems will also need to contend with overarching ethical issues facing future “smart cities,” such as data privacy and cybersecurity (Eggiman et al., 2017; Goodman, 2020).

3.6 Limitations

Our study design entailed several simplifying assumptions that could limit its generalizability. First, we chose a relatively large tank size in order to maximize the amount of water that could be stored and thereby available to satisfy demand during long antecedent dry periods. Stormwater capture systems of this scale (and larger) have been proposed and constructed in

many urban areas to address CSOs (City of Alexandria, VA, 2015; DC Water, 2020; Hopkins et al., 2018; Wu et al., 2016). Absent the regulatory pressure of the Clean Water Act, however, cities have less incentive to invest in expensive, large-scale stormwater storage systems. At the present unit cost for imported water in Los Angeles (\$1500 per acre-foot), it would cost roughly \$12,000 to fill our 10,000 m³-tank (Porse et al., 2018), a miniscule amount compared to the \$10M investment required for tank construction. However, if the main goal is runoff capture for environmental benefit, the cost of building stormwater capture systems may be less of a constraint, particularly as RTC technology improves. For example, a modeling study by Xu et al. (2020) found that increasing an RTC system's forecast lead time from one to seven days provided better flood protection than increasing tank capacity.

Second, we assumed that RTC-1 and RTC-2 had perfect knowledge of the upcoming weather forecast. The assumption of perfect forecasts is commonly used in RTC modeling studies (e.g., Garofalo et al. 2017; Roman et al., 2017), and a better understanding of the role of forecast accuracy has been cited as a key knowledge gap for RTC implementation (Kerkez et al., 2016). RTC systems with imperfect weather knowledge can outperform passive systems in terms of runoff capture (Xu et al., 2020), but the opposite may occur for water supply. With an imperfect forecast, the tank may release more water than necessary, reducing the volume available in storage to supply demand (Xu et al., 2018).

Finally, we assumed a seasonally periodic demand profile. The daily demand is included in the calculations for the volume of water to release pre-storm, with the goal of not releasing water that could have been used to satisfy demand one or two days in the future. If the daily water demand is variable and unpredictable (e.g., irregularly used for vehicle washing), then RTC systems cannot factor demand into their pre-storm release algorithms.

3.7 Management Implications

Overall, our analysis suggests that even perfectly smart stormwater systems (as represented here by control systems with perfect knowledge of the weather one or two days in the future) have their limits. Although engineers can incorporate safety factors into a tank's design (such as tank size or RTC pre-storm release algorithm), they cannot control the weather, and it is important to delineate how regional rainfall patterns affect smart stormwater infrastructure outcomes.

Southern California's uneven rainfall results in less demand satisfied and less runoff captured, relative to a counterfactual scenario with more evenly distributed rainfall. RTC technology increases the fraction of runoff captured, but does not increase the percent of human water demand satisfied in either precipitation scenario. By comparing the PDFs of human and environmental benefits conditioned on wet versus dry years, we bracket the range of operating conditions likely to be achieved in practice—important information for cost-benefit analysis of RTC implementation, for example to support EIB financing of stormwater capture. An RTC tank alone, even with perfect knowledge of the weather, cannot overcome the seasonality of rainfall in Southern California and reliably satisfy more than 50% of demand. This outcome might be even more pronounced for future rainfall scenarios, as recent research has suggested that climate change will result in slightly more precipitation concentrated during California's peak winter months, and less rainfall occurring in fall and spring (Swain et al., 2018). Stormwater RTC is likely to be more beneficial if used to enhance a distributed regional network of solutions including spreading basins, green stormwater infrastructure, and storage tanks. Future stormwater RTC implementation can also become smarter by ensuring that the local community is collaboratively involved in setting the goals for the RTC system, and by taking into account the social, political, and environmental context of the RTC system.

Chapter 5

Conclusion

The combination of studies presented in this dissertation, encompassing experimental fieldwork and rigorous modeling at multiple scales, demonstrates new solutions and possibilities for urban stormwater management. Clean bed filtration theory, in conjunction with other characteristics such as antecedent dry period and plant type, provides useful insight into predicting biofilter pollutant removal. The application of unsteady transit time distribution theory to biofilters provides a novel modeling framework for understanding how changing distributions of water age in outflow and storage affect biofilter outcomes. Finally, context-specific implementation of stormwater real-time control systems can help capture runoff and improve water supply for water-scarce areas, with some important limitations.

This dissertation also opens the door to several future research possibilities. First, the experiments described in Chapter 3 were carried out with an interdisciplinary team of microbiologists, soil ecologists, and chemists interested in many different aspects of biofilter performance. The 2019 bromide-spiked storm event was also spiked with raw sewage so that team members could investigate several different stormwater pollutants under transient flow conditions, including pathogens and microplastics. My collaborators are now in the process of analyzing their experimental results to quantify nitrogen transport and removal (including conversion to nitrous oxide, a potent greenhouse gas), heavy metal transport and sequestration, and pathogen removal, using the unsteady TTD approach developed in Chapter 3 as a common framework.

Future studies should also investigate how unsteady TTD theory can inform the application of RTC to green stormwater infrastructure systems, specifically asking: how can RTC optimize pollutant removal by altering biofilter transit time distributions? The modeling framework developed in this dissertation is a starting point to explore how systematic and real-time manipulation of the unsteady TTD can enhance or diminish biofilter performance over a single storm or over the course of several storms. For example, a TTD in which a large fraction of water passes through the biofilter quickly may result in less pollutant removal than one in which a large fraction of water spends a long time in the biofilter (although this could result in more biofilter overflow). RTC systems could enhance biofilter performance by controlling the biofilter inflow, outflow, or both. This would require a dynamic control system that optimizes the TTD for pollutant removal while also accounting for factors such as the storm intensity, antecedent dry period, evapotranspiration, and the specific pollutants of interest. The idea is along similar lines as the RTC of stormwater ponds to co-optimize nitrate removal and flood control benefits, however the fact that biofilters are a porous media make the system inherently more theoretically challenging.

The combination of RTC and TTD theory could also be investigated at scales beyond individual biofilters. For example, a large stormwater capture tank (like the one described in Chapter 4) could use RTC to release captured runoff to multiple biofilters, in accordance with optimal biofilter TTDs for pollutant removal. The combination of RTC and TTD theory could be further upscaled to the watershed or city scale with an integrated network of stormwater capture and natural treatment systems. “Real-time distributed control,” in conjunction with TTD theory distributed across various hydrologic units, would allow for co-optimization of runoff capture, pollutant removal, and water supply benefits on a broad scale.

Finally, as described in Chapter 4, the costs and benefits of deploying stormwater RTC infrastructure are context dependent. While Chapter 4 explores how a RTC system might operate to provide human and environmental benefits on the UCI campus, future research should evaluate stormwater RTC systems from a convergent socio-eco-hydrological system perspective. This would allow for a more systematic approach to map the various feedback loops, stakeholders, and structures that influence stormwater management and decisions at UCI, or any other location of interest. By prioritizing community engagement and blending the technology (data-driven hydrologic simulations, probability theory, and RTC technology) with socio-ecological context (practical regulatory, environmental, and economic constraints), stakeholders can better maximize the hydrological, ecological, and social benefits of stormwater systems.

References

Chapter 1 References

Afrooz, A. R. M. N.; Boehm, A. B. Effects of submerged zone, media aging, and antecedent dry period on the performance of biochar-amended biofilters in removing fecal indicators and nutrients from natural stormwater. *Ecol. Eng.* **2017**, *102*, 320-330.

Ahn, J.H.; Grant, S.B.; Surbeck, C.Q.; Digiacomo, P.M.; Nezlin, N.P.; Jiang, S.C. Coastal water quality impact of stormwater runoff from an urban watershed in Southern California. *Environ. Sci. Technol.* **2005**, *39* (16), 5940-5953.

Ali, M.; Fiori, A.; Russo, D. A comparison of travel-time based catchment transport models, with application to numerical experiments. *J. Hydrol.* **2014**, *511*, 605-618.

Askarizadeh, A.; Rippey, M. A.; Fletcher, T. D.; Feldman, D. L.; Peng, J.; Bowler, P.; Mehring, A. S.; Winfrey, B. K.; Vrugt, J. A.; AghaKouchak, A.; et al. From Rain Tanks to Catchments: Use of Low-Impact Development To Address Hydrologic Symptoms of the Urban Stream Syndrome. *Environ. Sci. Technol.* **2015**, *49* (19), 11264–11280.

Barnes, C.J.; Bonell, M. Application of Unit Hydrograph Techniques to Solute Transport in Catchments. *Hydrol. Proc.* **1996**, *10*, 793-802.

Bartos, M.; Wong, B.; Kerkez, B. Open storm: a complete framework for sensing and control of urban watersheds. *Environ. Sci.: Water Res. Technol.* **2018**, *4* (3), 346-358.

Burns, M. J.; Fletcher, T. D.; Walsh, C. J.; Ladson, A. R.; Hatt, B. E. Hydrologic shortcomings of conventional urban stormwater management and opportunities for reform. *Landsc. Urban Plan.* **2012**, *105* (3), 230–240.

Campisano, A.; Creaco, E.; Modica, C. Application of Real-Time Control Techniques to Reduce Water Volume Discharges from Quality-Oriented CSO Devices. *J. Environ. Eng.* **2016**, *142* (1), 04015049.

Carpenter, J. F.; Vallet, B.; Pelletier, G.; Lessard, P. Vanrolleghem, P. A. Pollutant removal efficiency of a retrofitted stormwater detention pond. *Water Qual. Res. J. Can.* **2014**, *49* (2), 124-134.

Clar, M.L.; Barfield, B.J.; O'Connor, T.P. Stormwater Best Mangement Practice Design Guide Volume 2: Vegetative Biofilters; EPA/600/R-04/121A; U.S. Environmental Protection Agency: Washington, DC, **2004**.

Cousins, J. J. Remaking stormwater as a resource: Technology, law, and citizenship. *Wiley Interdiscip. Rev.: Water* **2018**, 5 (5).

Eggiman, S.; Mutzner, L.; Wani, O.; Schneider, M. Y.; Spuhler, D.; de Vitry, M. M.; Beutler, P.; Maurer, M. The Potential of Knowing More: A Review of Data-Driven Urban Water Management. *Environ. Sci. Technol.* **2017**, 51 (5), 2538-2553.

Fletcher, T.D.; Deletic, A.; Mitchell, V.G.; Hatt, B.E. Reuse of urban runoff in Australia: A review of recent advances and remaining challenges. *J. Environ. Qual.* **2008** 37, 116-127.

Gaborit, E.; Anctil, F.; Pelletier, G.; Vanrolleghem, P. A. Exploring forecast-based management strategies for stormwater detention ponds. *Urban Water J.* **2016**, 13 (8), 841-851.

Gaborit, E.; Muschalla, D.; Vallet, B.; Vanrolleghem, P. A.; Anctil, F. Improving the performance of stormwater detention basins by real-time control using rainfall forecasts. *Urban Water J.* **2013**, 10 (4), 230-246.

Gaffield, S. J.; Goo, R. L.; Richards, L. A.; Jackson, R. J. Public Health Effects of Inadequately Managed Stormwater Runoff. *Am. J. Public Health* **2003**, 93 (9), 1527-1533.

Garofalo, G.; Giordano, A.; Piro, P.; Spezzano, G.; Vinci, A. A distributed real-time approach for mitigating CSO and flooding in urban drainage systems. *J. Network Comput. Appl.* **2017**, 78, 30-42.

Given, S.; Pendleton, L.H.; Boehm, A.B. Regional public health cost estimates of contaminated coastal waters: A case study of gastroenteritis at Southern California Beaches. *Environ. Sci. Technol.* **2006**, 40 (16), 4851-4858.

Gleick, P. H. Transitions to freshwater sustainability. *Proc. Natl. Acad. Sci. U. S. A.* **2018**, 115 (36), 8863-8871.

Grant, S.B.; Fletcher, T.D.; Feldman, D.; Saphores, J.-D.; Cook, P.L.M.; Stewardson, M.; Low, K.; Burry, K.; Hamilton, A.J. Adapting urban water systems to a changing climate: Lessons from the Millennium Drought in Southeast Australia. *Environ. Sci. Technol.* **2013** 47, 10727-10734.

Grant, S. B.; Saphores, J.-D.; Feldman, D. L.; Hamilton, A. J.; Fletcher, T. D.; Cook, P. L. M.; Stewardson, M.; Sanders, B. F.; Levin, L. A.; Ambrose, R. F.; et al. Taking the “Waste” Out of “Wastewater” for Human Water Security and Ecosystem Sustainability. *Science* **2012**, 337 (6095), 681–686.

Grebel, J. E.; Mohanty, S. K.; Torkelson, A. A.; Boehm, A. B.; Higgins, C. P.; Maxwell, R. M.; Nelson, K. L.; Sedlak, D. L. Engineered Infiltration Systems for Urban Stormwater Reclamation. *Environ. Eng. Sci.* **2013**, 30 (8), 437–454.

Hofer, T.; Montserrat, A.; Gruber, G.; Gamerith, V.; Corominas, L.; Muschalla, D. A robust and accurate surrogate method for monitoring the frequency and duration of combined sewer overflows. *Environ. Monit. Assess.* **2018**, *190*, 209.

Hrachowitz, M.; Benettin, P.; van Breukelen, B. M.; Fovet, O.; Howden, N. J. K.; Ruiz, L.; van der Velde, Y.; Wade, A. J. Transit times – the link between hydrology and water quality at the catchment scale. *WIREs Water*. **2016**, *3*, 629-657.

Jacopin, C.; Lucas, E.; Desbordes, M.; Bourgoigne, P. Optimisation of operational management practices for the detention basins. *Water Sci. Technol.* **2001**, *44* (2-3), 277-285.

Jiang, S. C.; Lim, K.; Huang, X.; McCarthy, D.; Hamilton, A. J. Human and environmental health risks and benefits associated with use of urban stormwater. *WIREs Water* **2015**, *2*, 683-699.

Kerkez, B.; Gruden, C.; Lewis, M.; Montestruque, L.; Quigley, M.; Wong, B.; Bedig, A.; Kertesz, R.; Braun, T.; Cadwalader, O.; Poresky, A.; Pak, C. Smarter Stormwater Systems. *Environ. Sci. Technol.* **2016**, *50* (14), 7267-7273.

Kim, M.; Pangle, L. A.; Cardoso, C.; Lora, M.; Volkmann, T. H. M.; Wang, Y.; Harman, C. J.; Troch, P. A. Transit time distributions and StorAge Selection functions in a sloping soil lysimeter with time-varying flow paths: Direct observation of internal and external transport variability. *Water Resour. Res.* **2016**, *52*, 7105-7129.

Kirchner, J. W.; Feng, X.; Neal, C. Catchment-scale advection and dispersion as a mechanism for fractal scaling in stream tracer concentrations. *J. Hydrol.* **2001**, *254*, 82-101.

Lim, K.; Hamilton, A. J.; Jiang, S. C. Assessment of public health risk associated with viral contamination in harvested urban stormwater for domestic applications. *Sci. Total Environ.* **2015**, *523*, 95-108.

Lim K.; Jiang, S. C. Reevaluation of health risk benchmark for sustainable water practice through risk analysis of rooftop-harvested rainwater. *Water Res.* **2013**, *47*, 7273-7286.

Lund, N. S. V.; Falk, A. K. V.; Borup, M.; Madsen, H.; Mikkelsen, P. S. Model predictive control of urban drainage systems: A review and perspective towards smart real-time water management. *Crit. Rev. Environ. Sci. Technol.* **2018**, *48* (3), 279-339.

National Academies, Water Science and Technology Board, National Research Council. *Urban Stormwater Management in the United States*, The National Academies Press: Washington, DC, 2009.

Payne, E.G.I., Hatt, B.E., Deletic, A., Dobbie, M.F., McCarthy, D.T. and Chandrasena, G.I., 2015. Adoption Guidelines for Stormwater Biofiltration Systems - Summary Report, Melbourne, Australia: Cooperative Research Centre for Water Sensitive Cities.

Reeves, R.L.; Grant, S.B.; Mrse, R.D.; Oancea, C.M.C.; Sanders, B.F.; Boehm, A.B. Scaling and management of fecal indicator bacteria in runoff from a coastal urban watershed in Southern California. *Environ. Sci. Technol.* **2004**, *38* (9), 2637-2648.

Romero-Lankao, P.; Norton, R. Interdependencies and Risk to People and Critical Food, Energy, and Water Systems: 2013 Flood, Boulder, Colorado, USA. *Earth's Future*. **2018**, *6*, 1616-1629.

Shortle, J. S.; Horan, R. D. The Economics of Nonpoint Pollution Control. *J. Econ. Surveys* **2001**, *15* (3), 255-289.

US EPA. *Results of the Nationwide Urban Runoff Program*. Water Planning Division, PB 84-185552. EPA: Washington, DC, 1983.

US EPA. *Smart Data Infrastructure for Wet Weather Control and Decision Support*. Office of Wastewater Management, 830-B-17-004. EPA: Washington, DC, 2018.

Walsh, C.J.; Fletcher, T.D.; Burns, M.J. Urban stormwater runoff: A new class of environmental flow problem. *PLOS One* **2012**, *7*, e45814.

Walsh, C. J.; Roy, A. H.; Feminella, J. W.; Cottingham, P. D.; Groffman, P. M.; Morgan, R. P. The urban stream syndrome: current knowledge and the search for a cure. *J. North Am. Benthol. Soc.* **2005**, *24*, 706–723.

Wong, T. H. F. Water sensitive urban design - the journey thus far. *Aust. J. Water Resour.* **2006**, *10* (3), 213–222.

Yazdanfar, Z.; Sharma, A. Urban drainage system planning and design – challenges with climate change and urbanization: a review. *Water Sci. Technol.* **2015**, *72* (2), 165-179.

Zhang, L.; Seagren, E. A.; Davis, A. P.; Karns, J. S. Long-Term Sustainability of Escherichia Coli Removal in Conventional Bioretention Media. *J. Environ. Eng.* **2011**, *137* (8), 669-677.

Chapter 2 References

- [1] Walsh, C. J.; Roy, A. H.; Feminella, J. W.; Cottingham, P. D.; Groffman, P. M.; Morgan, R. P. The urban stream syndrome: current knowledge and the search for a cure. *J. North Am. Benthol. Soc.* **2005**, *24*, 706–723.
- [2] Field, R.; Pitt, R. E.; Fan, C.-Y.; Heaney, J. P.; Stinson, M. K.; DeGuida, R. N.; Perdek, J. M.; Borst, M.; Hsu, K. F. Urban Wet-Weather Flows. *Water Environ. Res.* **1997**, *69* (4), 426–444.
- [3] Howarth, R. W.; Sharpley, A.; Walker, D. Sources of nutrient pollution to coastal waters in the United States: Implications for achieving coastal water quality goals. *Estuaries* **2002**, *25* (4), 656–676.
- [4] EPA, **1983**. Results of the Nationwide Urban Runoff Program. Water Planning Division, PB 84-185552. Washington, DC: EPA.
- [5] Fletcher, T.D.; Deletic, A.; Mitchell, V.G.; Hatt, B.E. Reuse of urban runoff in Australia: A review of recent advances and remaining challenges. *J. Environ. Qual.* **2008** *37*, 116-127.
- [6] Grant, S.B.; Fletcher, T.D.; Feldman, D.; Saphores, J.-D.; Cook, P.L.M.; Stewardson, M.; Low, K.; Burry, K.; Hamilton, A.J. Adapting urban water systems to a changing climate: Lessons from the Millennium Drought in Southeast Australia. *Environ. Sci. Technol.* **2013** *47*, 10727-10734.
- [7] Askarizadeh, A.; Rippy, M. A.; Fletcher, T. D.; Feldman, D. L.; Peng, J.; Bowler, P.; Mehring, A. S.; Winfrey, B. K.; Vrugt, J. A.; AghaKouchak, A.; et al. From Rain Tanks to Catchments: Use of Low-Impact Development To Address Hydrologic Symptoms of the Urban Stream Syndrome. *Environ. Sci. Technol.* **2015**, *49* (19), 11264–11280.
- [8] Walsh, C.J.; Fletcher, T.D.; Burns, M.J. Urban stormwater runoff: A new class of environmental flow problem. *PLOS One* **2012**, *7* (9), e45814.
- [9] Grant, S. B.; Saphores, J.-D.; Feldman, D. L.; Hamilton, A. J.; Fletcher, T. D.; Cook, P. L. M.; Stewardson, M.; Sanders, B. F.; Levin, L. A.; Ambrose, R. F.; et al. Taking the “Waste” Out of “Wastewater” for Human Water Security and Ecosystem Sustainability. *Science* **2012**, *337* (6095), 681–686.
- [10] Jiang, S. C.; Lim, K.; Huang, X.; McCarthy, D.; Hamilton, A. J. Human and environmental health risks and benefits associated with use of urban stormwater. *WIREs Water* **2015**, *2*, 683-699.
- [11] Lim, K.; Hamilton, A. J.; Jiang, S. C. Assessment of public health risk associated with viral contamination in harvested urban stormwater for domestic applications. *Sci. Total Environ.* **2015**, *523*, 95-108.

- [12] Payne, E.G.I., Hatt, B.E., Deletic, A., Dobbie, M.F., McCarthy, D.T. and Chandrasena, G.I., **2015**. Adoption Guidelines for Stormwater Biofiltration Systems - Summary Report, Melbourne, Australia: Cooperative Research Centre for Water Sensitive Cities.
- [13] Clar, M.L.; Barfield, B.J.; O'Connor, T.P. Stormwater Best Mangement Practice Design Guide Volume 2: Vegetative Biofilters; EPA/600/R-04/121A; U.S. Environmental Protection Agency: Washington, DC, **2004**.
- [14] Wong, T. H. F. Water sensitive urban design - the journey thus far. *Aust. J. Water Resour.* **2006**, *10* (3), 213–222.
- [15] Burns, M. J.; Fletcher, T. D.; Walsh, C. J.; Ladson, A. R.; Hatt, B. E. Hydrologic shortcomings of conventional urban stormwater management and opportunities for reform. *Landsc. Urban Plan.* **2012**, *105* (3), 230–240.
- [16] Chandrasena, G. I.; Pham, T.; Payne, E. G.; Deletic, A.; McCarthy, D. T. *E. coli* removal in laboratory scale stormwater biofilters: Influence of vegetation and submerged zone. *J. Hydrol.* **2014**, *519*, 814–822.
- [17] Li, Y. L.; Deletic, A.; Alcazar, L.; Bratieres, K.; Fletcher, T. D.; McCarthy, D. Removal of *Clostridium perfringens*, *Escherichia coli* and F-RNA coliphages by stormwater biofilters. *Ecol. Eng.* **2012**, *49*, 137-145.
- [18] Mohanty, S. K.; Torkelson, A. A.; Dodd, H.; Nelson, K. L.; Boehm, A. B. Engineering Solutions to Improve the Removal of Fecal Indicator Bacteria by Bioinfiltration Systems during Intermittent Flow of Stormwater. *Environ. Sci. Technol.* **2013**, *47* (19), 10791–10798.
- [19] Zhang, L.; Seagren, E.; Davis, A.; Karns, J. Long-Term Sustainability of *Escherichia Coli* Removal in Conventional Bioretention Media. *J. Environ. Eng.* **2011**, *137* (8), 669–677.
- [20] Chandrasena, G. I.; Deletic, A.; Ellerton, J.; McCarthy, D. T. Evaluating *Escherichia coli* removal performance in stormwater biofilters: a laboratory-scale study. *Water Sci. Technol.* **2012**, *66*, 1132–1138.
- [21] Mohanty, S. K.; Boehm, A. B. *Escherichia coli* Removal in Biochar-Augmented Biofilter: Effect of Infiltration Rate, Initial Bacterial Concentration, Biochar Particle Size, and Presence of Compost. *Environ. Sci. Technol.* **2013**, *48*(19), 11535-11542.
- [22] Hathaway, J. M.; Hunt, W. F.; Graves, A. K.; Wright, J. D. Field Evaluation of Bioretention Indicator Bacteria Sequestration in Wilmington, North Carolina. *J. Environ. Eng.* **2011**, *137*(12), 1103-1113.
- [23] Prüss, A. Review of epidemiological studies on health effects from exposure to recreational water. *Int. J. Epidemiol.* **1998**, *27* (1), 1–9.

- [24] Haile, R. W.; Witte, J. S.; Gold, M.; Cressey, R.; McGee, C.; Millikan, R. C.; Glasser, A.; Harawa, N.; Ervin, C.; Harmon, P.; et al. The health effects of swimming in ocean water contaminated by storm drain runoff. *Epidemiol. Camb. Mass* **1999**, *10* (4), 355–363.
- [25] Sidhu, J. P. S.; Ahmed, W.; Gernjak, W.; Aryal, R.; McCarthy, D.; Palmer, A.; Kolotelo, P.; Toze, S. Sewage pollution in urban stormwater runoff as evident from the widespread presence of multiple microbial and chemical source tracking markers. *Sci. Total Environ.* **2013**, *463-464*, 488–496.
- [26] Grebel, J. E.; Mohanty, S. K.; Torkelson, A. A.; Boehm, A. B.; Higgins, C. P.; Maxwell, R. M.; Nelson, K. L.; Sedlak, D. L. Engineered Infiltration Systems for Urban Stormwater Reclamation. *Environ. Eng. Sci.* **2013**, *30* (8), 437–454.
- [27] Ahn, J.H.; Grant, S.B.; Surbeck, C.Q.; Digiacomio, P.M.; Nezhlin, N.P.; Jiang, S.C. Coastal water quality impact of stormwater runoff from an urban watershed in Southern California. *Environ. Sci. Technol.* **2005**, *39* (16), 5940-5953.
- [28] Reeves, R.L.; Grant, S.B.; Mrse, R.D.; Oancea, C.M.C.; Sanders, B.F.; Boehm, A.B. Scaling and management of fecal indicator bacteria in runoff from a coastal urban watershed in Southern California. *Environ. Sci. Technol.* **2004**, *38* (9), 2637-2648.
- [29] EPA, **2007**. Total Maximum Daily Loads with Stormwater Sources: A Summary of 17 TMDLs, EPA 841-R-07-002. Washington, DC: EPA.
- [30] Given, S.; Pendleton, L.H.; Boehm, A.B. Regional public health cost estimates of contaminated coastal waters: A case study of gastroenteritis at Southern California Beaches. *Environ. Sci. Technol.* **2006**, *40* (16), 4851-4858.
- [31] Pendleton, L. The economics of using ocean observing systems to improve beach closure policy. *Coastal Management* **2008**, *36* (2), 165-178.
- [32] Point Loma Nazarene University, **2013**: Meeting Water Quality Standards for San Diego's Recreational Waters: A Cost Benefit Analysis, Fermanian Business and Economic Institute, San Diego, CA.
- [33] Davis, A.P.; Hunt, W.F.; Traver, R.G.; Clar, M. Bioretention technology: Overview of current practice and future needs. *J. Environ. Eng.* **2009**, *135* (3), 109-117.
- [34] Rippey, M. A. Meeting the criteria: linking biofilter design to fecal indicator bacteria removal. *WIREs Water*. **2015**, *2*, 577-592.
- [35] Yao, K.-M.; Habibian, M. T.; O'Melia, C. R. Water and waste water filtration: Concepts and applications. *Environ. Sci. Technol.* **1971**, *5* (11), 1105–1112.
- [36] Logan, B. E.; Jewett, D. G.; Arnold, R. G.; Bouwer, E. J.; O'Melia, C. R. Clarification of Clean-Bed Filtration Models. *J. Environ. Eng.* **1995**, *121*(12), 869-873.

- [37] Zhang, L.; Seagren, E. A.; Davis, A. P.; Karns, J. S. The Capture and Destruction of *Escherichia coli* from Simulated Urban Runoff Using Conventional Bioretention Media and Iron Oxide-coated Sand. *Water Environ. Res.* **2010**, 82, 701–714.
- [38] Peng, J.; Cao, Y.; Rippey, M. A.; Afrooz, A. R. M. N.; Grant, S. B. Indicator and Pathogen Removal by Low Impact Development Best Management Practices. *Water* **2016**, 8 (12), 600.
- [39] Chandrasena, G. I.; Deletic, A.; McCarthy, D. T. Evaluating *Escherichia coli* removal performance in stormwater biofilters: a preliminary modeling approach. *Water Sci. Technol.* **2013**, 67, 2467-2475.
- [40] Khatiwada, N. R.; Polprasert, C. Kinetics of Fecal Coliform Removal in Constructed Wetlands. *Wat. Sci. Technol.* **1999**, 40 (3), 109-116.
- [41] Bradford, S. A.; Bettahar, M.; Simunek, J.; van Genuchten, M. T. Straining and Attachment of Colloids in Physically Heterogeneous Porous Media. *Vadose Zone J.* **2004**, 3, 384-394.
- [42] Tufenkji, N. Modeling microbial transport in porous media: Traditional approaches and recent developments. *Adv. Wat. Resour.* **2007**, 30, 1455-1469.
- [43] Duncan, H. P. Urban Stormwater Quality: A Statistical Overview. Cooperative Research Centre for Catchment Hydrology, Melbourne, Australia, **1999**.
- [44] Ambrose, R. F.; Winfrey, B. K. Comparison of stormwater biofiltration systems in Southeast Australia and Southern California. *WIREs Water* **2015**, 2, 131-146.
- [45] Facility for Advancing Water Biofiltration (FAWB). Adoption Guidelines for Stormwater Bioinfiltration Systems. Monash University, Melbourne, Australia. **2009**, 1-38.
- [46] Han, Y.; Lau, S.; Kayhanian, M.; Stenstrom, M. K. Characteristics of Highway Stormwater Runoff. *Wat. Environ. Res.* **2006**, 78 (12), 2377-2388.
- [47] Levenspiel, O. *Chemical Reaction Engineering*, Wiley: New York, U.S., 1972.
- [48] Vrugt, J.A.; ter Braak, C.G.F.; Diks, C.G.H.; Higdon, D.; Robinson, B.A.; Hyman, J.M. Accelerating Markov chain Monte Carlo simulation by differential evolution with self-adaptive randomized subspace sampling. *Int. J. Nonlinear Sci. Numer. Simul.* **2009**, 10, 273-290.
- [49] Vrugt, J. A. Markov chain Monte Carlo simulation using the DREAM software package: Theory, concepts, and MATLAB implementation. *Environ. Model. Softw.* **2016**, 75, 273–316.
- [50] Wehner, J.F.; Wilhelm, R.H. Boundary conditions of flow reactor. *Chem. Eng. Sci.* **1956** 6, 89-93.

- [51] Tufenkji, N.; Elimelech, M. Correlation Equation for Predicting Single-Collector Efficiency in Physicochemical Filtration in Saturated Porous Media. *Environ. Sci. Technol.* **2004**, *38* (2), 529–536.
- [52] R core team (2013). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-90051-07-0, URL <http://www.R-project.org/>.
- [53] Surbeck, C.Q.; Jiang, S.C.; Grant, S.B. Ecological control of fecal indicator bacteria in an urban stream. *Environ. Sci. Technol.* **2010**, *44* (2), 631-637.
- [54] Zuur, A. F.; Ieno, E. N.; Elphick, C. S. A protocol for data exploration to avoid common statistical problems. *Method. Ecol. Evol.* **2010**, *1*, 3-14.
- [55] Schwarz, G. Estimating the dimension of a model. *Ann. Statist.* **1978**, *6*, 461-464.
- [56] Hawkins, D. M.; Basak, S. C.; Mills, D. Assessing model fit by cross-validation. *J. Chem. Inf. Comput. Sci.* **2003**, *43*, 579-586.
- [57] Gromping, U. Relative Importance for Linear Regression in R: The Package relaimpo. *J. Stat. Softw.* **2006**, *17* (1), 1-27.
- [58] Blecken, G-T.; Zinger, Y.; Deletic, A.; Fletcher, T. D.; Viklander, M. Influence of intermittent wetting and drying conditions on heavy metal removal by stormwater biofilters. *Water Research.* **2009**, *43*, 4590-4598.
- [59] Payne, E. G. I.; Pham, T.; Cook, P. L. M.; Fletcher, T. D.; Hatt, B. E.; Deletic, A. Biofilter design for effective nitrogen removal from stormwater – influence of plant species, inflow hydrology and use of a saturated zone. *Wat. Sci. Technol.* **2014**, *69* (6), 1312-1319.
- [60] Read, J.; Wevill, T.; Fletcher, T. D.; Deletic, A. Variation among plant species in pollutant removal from stormwater in biofiltration systems. *Water Res.* **2008**, *42*, 893-902.
- [61] Read, J.; Fletcher, T. D.; Wevill, T.; Deletic, A. Plant traits that enhance pollutant removal from stormwater in biofiltration systems. *Int. J. Phytoremediation* **2009**, *12*, 34-53.
- [62] Bonkowski, M.; Villenave, C.; Griffiths, B. Rhizosphere fauna: the functional and structural diversity of intimate interactions of soil fauna with plant roots. *Plant and Soil* **2009**, *321* (1), 213-233.
- [63] Afrooz, A.R.M.; Boehm, A.B. *Escherichia coli* removal in biochar-modified biofilters: effects of biofilm *PLOS One.* **2016**, *11* (12), e0167489.
- [64] Foppen, J. W.; Liem, Y.; Schijven, J. Effect of humic acid on the attachment of *Escherichia coli* in columns of goethite-coated sand. *Water Res.* **2008**, *42*, 211-219.

- [65] Archer, N. A. L.; Quinton, J. N.; Hess, T. M. Below-ground relationships of soil texture, roots and hydraulic conductivity in two-phase mosaic vegetation in South-east Spain. *J. Arid. Environ.* **2002**, *52*, 535-553.
- [66] Virahsawmy, H. K.; Stewardson, M. J.; Vietz, G.; Fletcher, T. D. Factors that affect the hydraulic performance of raingardens: implications for design and maintenance. *Wat. Sci. Technol.* **2014**, *69* (5), 982-988.
- [67] O'Melia, C. R.; Ali, W. The role of retained particles in deep bed filtration. *Progr. Water Technol.* **1978**, *10*, 167-182.
- [68] Belden, E.; Antos, M.; Morris, K.; Steele, N. L.C. Sustainable Infrastructure: The Elmer Avenue Neighborhood Retrofit. *Urban Coast*, **2012**, *3*(1), 92-100.
- [69] Kandra, H.; McCarthy, D.; Deletic, A. Assessment of the Impact of Stormwater Characteristics on Clogging in Stormwater Filters. *Water Resour. Manage.* **2015**, *29*(4), 1031-1048.
- [70] EPA, **2015**. Storm Water Management Model User's Manual Version 5.1, EPA 600/%-14/413b. Washington, DC: EPA.

Chapter 3 References

- Alikhani, J., Nietch, C., Jacobs, S., Shuster, B., & Massoudieh, A. (2020). Modeling and design scenario analysis of long-term monitored bioretention system for rainfall-runoff reduction to combined sewer in Cincinnati, OH. *Journal of Sustainable Water in the Built Environment*, 6(2), 04019016.
- Allen, R. G., Pereira, L. S., Raes, D., & Smith, M. (1998). Crop evapotranspiration – Guidelines for computing crop water requirements – FAO Irrigation and Drainage Paper 56. Food and Agriculture Organization of the United Nations.
- Al-Mashaqbeh, O., & McLaughlan, R. G. (2012) Non-equilibrium zinc uptake onto compost particles from synthetic stormwater. *Bioresource Technology*, 123, 242-248.
- Ambrose, R. F., & Winfrey, B. K. (2015). Comparison of stormwater biofiltration systems in Southeast Australia and Southern California. *WIREs Water*, 2, 131-146.
- Ang, A. H-S., & Tang, W. H. (2007) *Probability Concepts in Engineering: Emphasis on Applications to Civil and Environmental Engineering*, 2nd edition. Hoboken, NJ: John Wiley & Sons, Inc.
- Bedan, E. S., & Clausen, J. C. (2009). Stormwater Runoff Quality and Quantity from Traditional and Low Impact Development Watersheds. *Journal of the American Water Resources Association*, 45(4), 998-1008.
- Behroozi, A., Arora, M., Fletcher, T. D., & Western, A. W. (2020). Sorption and transport behavior of zinc in the soil; Implications for stormwater management. *Geoderma*, 367, 114243.
- BenDor, T. K., Shandas, V., Miles, B., Belt, K., & Olander, L. (2018). Ecosystem services and U.S. stormwater planning: An approach for improving urban stormwater decisions. *Environmental Science & Policy*, 88, 92-103.
- Benettin, P., & Bertuzzo, E. (2018). Tran-SAS v1.0: a numerical model to compute catchment-scale hydrologic transport using StorAge Selection functions. *Geoscientific Model Development*, 11, 1627-1639.
- Benettin, P., Bailey, S. W., Rinaldo, A., Likens, G. E., McGuire, K. J., & Botter, G. (2017). Young runoff fractions control streamwater age and solute concentration dynamics. *Hydrological Processes*, 31(16), 2982-2986.
- Benettin, P., Bailey, S. W., Campbell, J. L., Green, M. B., Rinaldo, A., Likens, G. E., McGuire, K. J., & Botter, G. (2015b). Linking water age and solute dynamics in streamflow at the Hubbard Brook Experimental Forest, NH, USA, *Water Resources Research*, 51, 9256–9272, doi:10.1002/2015WR017552.

- Benettin, P., Rinaldo, A., Botter, G. (2013) Kinematics of age mixing in advection-dispersion models. *Water Resources Research* 49, 8539-8551. doi:10.1002/2013WR014708
- Benettin, P., Rinaldo, A., & Botter, G. (2015a). Tracking residence times in hydrological systems: Forward and backward formulations. *Hydrological Processes*, 29(25), 5203-5213.
- Bertuzzo, E., Thomet, M., Botter, G., & Rinaldo, A. (2013). Catchment-scale herbicides transport: Theory and application. *Advances in Water Resources*, 52, 232-242.
- Boehm, A. B., Bell, C. D., Fitzgerald, N. J. M., Gallo, E., Higgins, C. P., Hogue, T. S., et al. (2020). Biochar-augmented biofilters to improve pollutant removal from stormwater – can they improve receiving water quality? *Environmental Science: Water Research & Technology*, 6, 1520-1537.
- Boivin, A., Simunek, J., Schiavon, M., & van Genuchten, M. (2006). Comparison of Pesticide Transport Processes in Three Tile-Drained Field Soils Using HYDRUS-2D. *Vadose Zone Journal*, 5(3), 838-849.
- Botter, G., Bertuzzo, E., & Rinaldo, A. (2011). Catchment residence and travel time distributions: The master equation. *Geophysical Research Letters*, 38(11), L11403. doi:10.1029/2011GL047666
- Brooks, K. N., Ffolliott, P. F., & Magner, J. A. (2013). *Hydrology and the Management of Watersheds* (4th Edition). Ames, IA: John Wiley & Sons, Inc.
- Brown, R. A., & Hunt, W. F. (2011). Underdrain configuration to enhance bioretention exfiltration to reduce pollutant loads. *Journal of Environmental Engineering*, 137(11), 1082-1091. [https://doi.org/10.1061/\(ASCE\)EE.1943-7870.0000437](https://doi.org/10.1061/(ASCE)EE.1943-7870.0000437)
- Browne, D., Deletic, A., Mudd, G. M., & Fletcher, T. D. (2008). A new saturated/unsaturated model for stormwater infiltration systems. *Hydrological Processes*, 22, 4838-4849.
- Canfield, D.E., Glazer, A.N., & Falkowski, P.G. (2010) The evolution and future of Earth's nitrogen cycle. *Science*, 330, 192-196.
- Chandrasena, G. I., Deletic, A., & McCarthy, D. T. (2014b). Survival of Escherichia coli in stormwater biofilters. *Environmental Science and Pollution Research*, 21(8), 5391-5401.
- Chandrasena, G. I., Pham, T., Payne, E. G. I., Deletic, A., & McCarthy, D. T. (2014a). E. coli removal in laboratory scale stormwater biofilters: Influence of vegetation and submerged zone. *Journal of Hydrology*, 519, 814-822.
- Chandrasena, G. I., Shirdashtzadeh, M., Li, Y. L., Deletic, A., Hathaway, J. M., & McCarthy, D. T. (2017). Retention and survival of E. coli in stormwater biofilters: Role of vegetation, rhizosphere microorganisms and antimicrobial filter media. *Ecological Engineering*, 102, 166-177.

Clar, M. L., Barfield, B. J., & O'Connor, T.P. (2004). Stormwater Best Mangement Practice Design Guide Volume 2: Vegetative Biofilters, EPA/600/R-04/121A, Washington, DC: U.S. Environmental Protection Agency.

Daly, E., Deletic, A., Hatt, B. E., & Fletcher, T. D. (2012). Modelling of stormwater biofilters under random hydrologic variability: a case study of a car park at Monash University, Victoria (Australia). *Hydrological Processes*, 26, 3416-3424.

Danesh-Yazdi, M., Klaus, J., Condon, L. E., & Maxwell, R. M. (2018). Bridging the gap between numerical solutions of travel time distributions and analytical storage selection functions. *Hydrological Processes*, 32(8), 1063-1076.

Davis, J.C. (2002), "Statistics and Data Analysis in Geology, 3rd Ed." John Wiley & Sons, Inc. New York, 638pp.

Davis, A. P. (2008). Field performance of bioretention: hydrology impacts. *Journal of Hydrologic Engineering*, 13(2), 90-95. DOI: 10.1061/(ASCE)1084-0699(2008)13:2(90)

Davis, A. P., Hunt, W. F., Traver, R. G., & Clar, M. (2009). Bioretention Technology: Overview of Current Practice and Future Needs. *Journal of Environmental Engineering*, 135(3), 109-117.

Dos Santos, D. R., Cambier, P., Mallmann, F. J. K., Labanowski, J., Lamy, I., Tessier, D., & van Oort, F. (2013). Prospective modeling with Hydrus-2D of 50 years Zn and Pb movements in low and moderately metal-contaminated agricultural soils. *Journal of Contaminant Hydrology*, 145, 54-66.

Engemann, K., Pedersen, C. B., Arge, L., Tsirogiannis, C., Mortensen, P. B., & Svenning, J. C. (2019). Residential green space in childhood is associated with lower risk of psychiatric disorders from adolescence into adulthood. *Proceedings of the National Academy of Sciences*, 116(11), 5188-5193.

eWater Ltd. (2020) Model for Urban Stormwater Improvement Conceptualization MUSICX. Bruce, ACT, Australia.

Feng, W., Hatt, B. E., McCarthy, D. T., Fletcher, T. D., & Deletic, A. (2012). Biofilters for Stormwater Harvesting: Understanding the Treatment Performance of Key Metals That Pose a Risk for Water Use. *Environmental Science & Technology*, 46(9), 5100-5108.

Garcia-Aljaro, C., Blanch, A. R., Campos, C., Jofre, J., & Lucena, F. (2018). Pathogens, faecal indicators and human specific microbial source-tracking markers in sewage. *Journal of Applied Microbiology*, 126, 701-717.

Grant, S.B., Saphores, J.D., Feldman, D.L., Hamilton, A.J., Fletcher, T.D. et al. (2012) Taking the 'Waste' out of 'Wastewater' for Human Water Security and Ecosystem Sustainability. *Science* 337, 681-686.

- Grant, S. B., Fletcher, T. D., Feldman, D., Saphores, J. D., Cook, P. L. M., Stewardson, M., et al. (2013). Adapting Urban Water Systems to a Changing Climate: Lessons from the Millennium Drought in Southeast Australia. *Environmental Science & Technology*, 47(19), 10727-10734.
- Grebel, J. E., Mohanty, S. K., Torkelson, A. A., Boehm, A. B., Higgins, C. P., Maxwell, R. M., et al. (2013). Engineered Infiltration Systems for Urban Stormwater Reclamation. *Environmental Engineering Science*, 30(8), 437-454.
- Green, W. H., & Ampt, G. A. (1911). Studies on Soil Physics, Part 1, The Flow of Air and Water through Soils. *Journal of Agricultural Science*, 4, 11-24.
- Harman, C. J. (2015). Time-variable transit time distributions and transport: Theory and application to storage-dependent transport of chloride in a watershed. *Water Resources Research*, 51, 1-30. doi:[10.1002/2014WR015707](https://doi.org/10.1002/2014WR015707)
- Harman, C. J. (2019). Age-Ranked Storage-Discharge Relations: A Unified Description of Spatially Lumped Flow and Water Age in Hydrologic Systems. *Water Resources Research*, 55(8), 7143-7165. doi:[10.1029/2017WR022304](https://doi.org/10.1029/2017WR022304)
- Hatt, B. E., Fletcher, T. D., & Deletic, A. (2009). Hydrologic and pollutant removal performance of stormwater biofiltration systems at the field scale. *Journal of Hydrology*, 365(3-4), 310-321.
- Henrichs, M., Welker, A., & Uhl, M. (2009). Modelling of biofilters for ammonium reduction in combined sewer overflow. *Water Science & Technology*, 60(3), 825-831.
- Hess, A., Wadzuk, B., & Welker, A. (2019). Predictive Evapotranspiration Equations in Rain Gardens. *Journal of Irrigation and Drainage Engineering*, 145(7), 04019010.
- Hillel, D. (2003). *Introduction to Environmental Soil Physics*. Cambridge, MA: Academic Press.
- Horel, A., Schiewer, S., & Misra, D. (2015). Effect of concentration gradients on biodegradation in bench-scale sand columns with HYDRUS modeling of hydrocarbon transport and degradation. *Environmental Science and Pollution Research*, 22, 13251-13262.
- Hrachowitz, M., Benettin, P., van Breukelen, B. M., Fovet, O., Howden, N. J. K., Ruiz, L., et al. (2016). Transit times – the link between hydrology and water quality at the catchment scale. *WIREs Water*, 3, 629-657.
- Jefferson, A. J., Bhaskar, A. S., Hopkins, K. G., Fanelli, R., Avellaneda, P. M., & McMillan, S. K. (2017). Stormwater management network effectiveness and implications for urban watershed function: A critical review. *Hydrological Processes*, 31(23), 4056-4080.
- Jiang, C., Li, J., Li, H., & Li, Y. (2019). Experiment and simulation of layered bioretention system for hydrological performance. *Journal of Water Reuse and Desalination*, 9(3), 319-329.

- Jiang, S., Pang, L., Buchan, G. D., Simunek, J., Noonan, M. J., & Close, M. E. (2010). Modeling water flow and bacterial transport in undisturbed lysimeters under irrigations of dairy shed effluent and water using HYDRUS-1D. *Water Research*, 44(4), 1050-1061.
- Keeler, B. L., Hamel, P., McPhearson, T., Hamann, M. H., Donahue, M. L., Meza Prado, K. A., et al. (2019). Socio-ecological and technological factors moderate the value of urban nature. *Nature Sustainability*, 2, 29-38.
- Kerkez, B., Gruden, C., Lewis, M., Montestruque, L., Quigley, M., Wong, B., et al. (2016). Smarter Stormwater Systems. *Environmental Science & Technology*, 50(14), 7267-7273.
- Kim, H., Seagren, E.A., & Davis, A.P (2003), Engineered bioretention for removal of nitrate from stormwater runoff, *Water Environment Research* 75(4), 355-367.
- Kim, M., Pangle, L. A., Cardoso, C., Lora, M., Volkmann, T. H. M., Wang, Y., Harman, C. J., & Troch, P. A. (2016). Transit time distributions and StorAge Selection functions in a sloping soil lysimeter with time-varying flow paths: Direct observation of internal and external transport variability, *Water Resources Research*, 52, 7105–7129, doi:10.1002/2016WR018620.
- Kirchner, J. W. (2009). Catchments as simple dynamical systems: Catchment characterization, rainfall-runoff modeling, and doing hydrology backward. *Water Resources Research*, 45, W02429. doi:10.1029/2008WR006912
- Kirchner, J. W. (2016). Aggregation in environmental systems-Part 1: Seasonal tracer cycles quantify young water fractions, but not mean transit times, in spatially heterogeneous catchments. *Hydrology and Earth System Sciences*, 20(1), 279-297.
- Kranner, B. P., Afrooz, A. R. M. N., Fitzgerald, N. J. M., & Boehm, A. B. (2019). Fecal indicator bacteria and virus removal in stormwater biofilters: Effects of biochar, media saturation, and field conditioning. *PLoS One*, 14(9), e0222719.
- Le Coustumer, S., Fletcher, T. D., Deletic, A., Barraud, S., & Lewis, J. F. (2009). Hydraulic performance of biofilter systems for stormwater management: Influences of design and operation. *Journal of Hydrology*, 376(1-2), 16-23.
- Le Coustumer, S., Fletcher, T. D., Deletic, A., Barraud, S., & Poelsma, P. (2012). The influence of design parameters on clogging of stormwater biofilters: A large-scale column study. *Water Research*, 46(20), 6743-6752.
- Lee, J. G., Borst, M., Brown, R. A., Rossman, L., Simon, M. A. (2015). Modeling the hydrologic processes of a permeable pavement system. *Journal of Hydrologic Engineering*, 20(5), 1-9.
- Lee, C. M., Lin, T. Y., Lin, C., Kohbodi, G. A., Bhatt, A., Lee, R., Jay, J. A. (2006). Persistence of fecal indicator bacteria in Santa Monica Bay beach sediments. *Water Research*, 40(14), 2593-2602.

- LeFevre, G. H., Paus, K. H., Natarajan, P., Gulliver, J. S., Novak, P. J., & Hozalski, R. M. (2015). Review of Dissolved Pollutants in Urban Storm Water and Their Removal and Fate in Bioretention Cells. *Journal of Environmental Engineering*, 141(1), 04014050.
- Levy, B. S., & Chambers, R. M. (1987). Bromide as a conservative tracer for soil-water studies. *Hydrological Processes*, 1(4), 385-389.
- Li, C., Fletcher, T. D., Duncan, H. P., & Burns, M. J. (2017). Can stormwater control measures restore altered urban flow regimes at the catchment scale? *Journal of Hydrology* 549, 631-653.
- Li, L., & Davis, A. P. (2014). Urban Stormwater Runoff Nitrogen Composition and Fate in Bioretention Systems. *Environmental Science & Technology*, 48(6), 3403-3410.
- Li, Y., Deletic, A., Alcazar, L., Bratieres, K., Fletcher, T. D., & McCarthy, D. T. (2012). Removal of *Clostridium perfringens*, *Escherichia coli* and F-RNA coliphages by stormwater biofilters. *Ecological Engineering*, 49, 137-145.
- Li, Y., McCarthy, D. T., & Deletic, A. (2016). *Escherichia coli* removal in copper-zeolite-integrated stormwater biofilters: Effect of vegetation, operational time, intermittent drying weather. *Ecological Engineering*, 90, 234-243.
- Lutz, S. R., Krieg, R., Müller, C., Zink, M., Knöller, K., Samaniego, L., & Merz, R. (2018). Spatial patterns of water age: Using young water fractions to improve the characterization of transit times in contrasting catchments. *Water Resources Research*, 54(7), 4767-4784. <https://doi.org/10.1029/2017WR022216>
- Massoudieh, A., Maghrebi, M., Kamrani, B., Nietch, C., Tryby, M., Aflaki, S., & Panguluri, S. (2017). A flexible modeling framework for hydraulic and water quality performance assessment of stormwater green infrastructure. *Environmental Modelling & Software*, 92, 57-73.
- McPhillips, L., Goodale, C., Walter, T. (2018) Nutrient leaching and greenhouse gas emissions in grassed detention and bioretention stormwater basins. *Journal of Sustainable Water in the Built Environment*, 4(1), doi: 10.1061/JSWBAY.0000837.
- Metzler, H., Muller, M., & Sierra, C. A. (2018). Transit-time and age distributions for nonlinear time-dependent compartmental systems. *Proceedings of the National Academy of Sciences*, 115(6), 1150-1155.
- Mohanty, S. K., & Boehm, A.B. (2014). *Escherichia coli* Removal in Biochar-Augmented Biofilter: Effect of Infiltration Rate, Initial Bacterial Concentration, Biochar Particle Size, and Presence of Compost. *Environmental Science & Technology*, 48(19) 11535-11542.
- National Academies of Sciences, Engineering, and Medicine. (2016). *Using Graywater and Stormwater to Enhance Local Water Supplies: An Assessment of Risks, Costs, and Benefits*. Washington, DC: The National Academies Press.

Niemi, A. J. (1977). Residence Time Distributions of Variable Flow Processes. *International Journal of Applied Radiation and Isotopes*, 28, 855-860.

Orange County Public Works (2017). Prop. 84 OC Public Works Glassell Campus Stormwater LID Retrofit Project Final Report PIN 24108. Orange, CA.

Parker, E. A., Rippey, M. A., Mehring, A. S., Winfrey, B. K., Ambrose, R. F., Levin, L. A., & Grant, S. B. (2017). Predictive Power of Clean Bed Filtration Theory for Fecal Indicator Bacteria Removal in Stormwater Biofilters. *Environmental Science & Technology*, 51(10), 5703-5712.

Payne, E. G. I., Hatt, B. E., Deletic, A., Dobbie, M. F., McCarthy, D. T., & Chandrasena, G. I. (2015). Adoption Guidelines for Stormwater Biofiltration Systems - Summary Report. Melbourne, Australia: Cooperative Research Centre for Water Sensitive Cities.

Payne, E. G. I., Pham, T., Cook, P. L. M., Fletcher, T. D., Hatt, B. E., & Deletic, A. (2014). Biofilter design for effective nitrogen removal from stormwater – influence of plant species, inflow hydrology and use of a saturated zone. *Water Science & Technology*, 69(6), 1312-1319.

Payne, E. G. I., Pham, T., Deletic, A., Hatt, B. E., Cook, P. L. M., & Fletcher, T. D. (2018). Which species? A decision-support tool to guide plant selection in stormwater biofilters. *Advances in Water Resources*, 113, 86-99.

Peng, J., Cao, Y., Rippey, M. A., Afrooz, A. R. M. N., Grant, S. B. (2016). Indicator and Pathogen Removal by Low Impact Development Best Management Practices. *Water* 8(12), 600.

Radcliffe, D., & Simunek, J. (2010). *Soil Physics with HYDRUS*. Boca Raton, FL: CRC Press.

Randelovic, A., Zhang, K., Jacimovic, N., McCarthy, D., & Deletic, A. (2016). Stormwater biofilter treatment model (MPiRe) for selected micro-pollutants. *Water Research*, 89, 180-191.

Raymond, C. M., Frantzeskaki, N., Kabisch, N., Berry, P., Breil, M., Nita, M. R., et al. (2017). A framework for assessing and implementing the co-benefits of nature-based solutions in urban areas. *Environmental Science & Policy*, 77, 15-24.

Read, J., Wevill, T., Fletcher, T., & Deletic, A. (2008). Variation among plant species in pollutant removal from stormwater in biofiltration systems. *Water Research*, 42(4-5), 893-902.

Read, J., Fletcher, T. D., Wevill, T., Deletic, A. (2009). Plant Traits that Enhance Pollutant Removal from Stormwater in Biofiltration Systems. *International Journal of Phytoremediation*, 12(1), 34-53.

Rinaldo, A., Benettin, P., Harman, C. J., Hrachowitz, M., McGuire, K. J., Van Der Velde, Y., Bertuzzo, E., & Botter, G. (2015). Storage selection functions: A coherent framework for quantifying how catchments store and release water and solutes. *Water Resources Research*, 51(6), 4840-4847. <https://doi.org/10.1002/2015WR017273>

- Rinaldo, A., Beven, K. J., Bertuzzo, E., Nicotina, L., Davies, J., Fiori, A., Russo, D., & Botter, G. (2011). Catchment travel time distributions and water flow in soils. *Water Resources Research*, 47, W07537. <https://doi.org/10.1029/2011WR010478>
- Rippy, M. A. (2015). Meeting the criteria: linking biofilter design to fecal indicator bacteria removal. *Wiley Interdisciplinary Reviews: Water*, 2(5), 577-592.
- Rodriguez, N. B., McGuire, K. J., & Klaus, J. (2018). Time-varying storage– Water age relationships in a catchment with a Mediterranean climate. *Water Resources Research*, 54, 3988–4008. <https://doi.org/10.1029/2017WR021964>
- Roy-Poirier, A., Champagne, P., & Filion, Y. (2010). Review of Bioretention System Research and Design: Past, Present, and Future. *Journal of Environmental Engineering* 136(9), 878-889.
- Rycciewicz-Borecki, M., McLean, J. E., & Dupont, R. R. (2017). Nitrogen and phosphorous mass balance, retention and uptake in six plant species grown in stormwater bioretention microcosms. *Ecological Engineering*, 99, 409-416.
- Saiers, J.E. & Lenhart, J.J. (2003). Colloid mobilization and transport within unsaturated porous media under transient-flow conditions. *Water Resour. Res.* 39(1), 1029, doi:10.1029/2002WR001370.
- Shen, P., Deletic, A., Urich, C., Chandrasena, G. I., & McCarthy, D. T. (2018). Stormwater biofilter treatment model for faecal microorganisms. *Science of the Total Environment* 630, 992-1002.
- Simunek, J., van Genuchten, M., & Sejna, M. (2008). Development and Applications of the HYDRUS and STANMOD Software Packages and Related Codes. *Vadose Zone Journal*, 7(2), 587-600.
- Smith, A. A., Tetzlaff, D., & Soulsby, C. (2018). On the Use of StorAge Selection Functions to Assess Time-Variant Travel Times in Lakes. *Water Resources Research*, 54, 5163-5185. <https://doi.org/10.1029/2017WR021242>
- Snodgrass, J. W., Moore, J., Lev, S. M., Casey, R. E., Ownby, D. R., Flora, R. F., & Izzo, G. (2017). Influence of Modern Stormwater Management Practices on Transport of Road Salt to Surface Waters. *Environmental Science & Technology*, 51(8), 4165-4172.
- Surbeck, C. Q., Jiang, S. C., & Grant, S. B. (2010). Ecological Control of Fecal Indicator Bacteria in an Urban Stream. *Environmental Science & Technology*, 44(2) 631-637.
- Trenouth, W. R., & Gharabaghi, B. (2015). Soil amendments for heavy metals removal from stormwater runoff discharging to environmentally sensitive areas. *Journal of Hydrology*, 529(3), 1478-1487.

Ulrich, B. A., Vignola, M., Edgehouse, K., Werner, D., & Higgins, C. P. (2017). Organic Carbon Amendments for Enhanced Biological Attenuation of Trace Organic Contaminants in Biochar-Amended Stormwater Biofilters. *Environmental Science & Technology*, 51(16), 9184-9193.

U. S. Environmental Protection Agency. (2018). 2017 Five-Year Review of the 2012 Recreational Water Quality Criteria. EPA-823-R-18-001. Washington, DC: Office of Water, US EPA.

Walsh, C. J., Booth, D. B., Burns, M. J., Fletcher, T. D., Hale, R. L., Hoang, L. N., et al. (2016). Principles for urban stormwater management to protect stream ecosystems. *Freshwater Science*, 35(1), 398-411.

Walsh, C.J., Fletcher, T.D., & Burns, M.J. (2012). Urban stormwater runoff: A new class of environmental flow problem. *PLoS One*, 7, e45814.

Walsh, C. J., Roy, A. H., Feminella, J. W., Cottingham, P. D., Groffman, P. M., & Morgan, R. P. (2005). The urban stream syndrome: current knowledge and the search for a cure. *Journal of the North American Benthological Society*, 24, 706–723.

Williams, J. R., Ouyang, Y., Chen, J., & Ravi, V. (1998). Estimation of Infiltration Rate in Vadose Zone: Application of Selected Mathematical Models Volume II. EPA/600/R-97/128b, Ada, OK: National Risk Management Research Laboratory, U.S. Environmental Protection Agency.

Winston, R. J., Dorsey, J. D., & Hunt, W. F. (2016). Quantifying volume reduction and peak flow mitigation for three bioretention cells in clay soils in northeast Ohio. *Science of the Total Environment*, 553, 83-95.

Wong, T. H. F. (2006). Water sensitive urban design – the journey thus far. *Australasian Journal of Water Resources*, 10 (3), 213-222.

Zhang, K., Randelovic, A., Deletic, A., Page, D., & McCarthy, D. T. (2019). Can we use a simple modeling tool to validate stormwater biofilters for herbicides treatment? *Urban Water Journal*, 16(6), 412-420.

Zhang, L., Seagren, E. A., Davis, A. P., & Karns, J. S. (2010). The Capture and Destruction of *Escherichia coli* from Simulated Urban Runoff Using Conventional Bioretention Media and Iron Oxide-coated Sand. *Water Environment Research*, 82(8), 701-714.

Zhao, L., Xia, J., Xu, C., Wang, Z., Sobkowiak, L., & Long, C. (2013). Evapotranspiration estimation methods in hydrological models. *Journal of Geographical Sciences*, 23(2), 359-369.

Chapter 4 References

- Ahn, J.H.; Grant, S.B.; Surbeck, C.Q.; Digiacomio, P.M.; Nezlin, N.P.; Jiang, S.C. Coastal water quality impact of stormwater runoff from an urban watershed in Southern California. *Environ. Sci. Technol.* **2005**, *39* (16), 5940-5953.
- Askarizadeh, A.; Rippey, M. A.; Fletcher, T. D.; Feldman, D. L.; Peng, J.; Bowler, P.; Mehring, A. S.; Winfrey, B. K.; Vrugt, J. A.; AghaKouchak, A.; et al. From Rain Tanks to Catchments: Use of Low-Impact Development To Address Hydrologic Symptoms of the Urban Stream Syndrome. *Environ. Sci. Technol.* **2015**, *49* (19), 11264–11280.
- Balboa, C. M. Accountability of Environmental Impact Bonds: The Future of Global Environmental Governance? *Glob. Environ. Polit.* **2016**, *16* (2), doi:10.1162/GLEP_a_00352.
- Bartos, M.; Wong, B.; Kerkez, B. Open storm: a complete framework for sensing and control of urban watersheds. *Environ. Sci.: Water Res. Technol.* **2018**, *4* (3), 346-358.
- Behzadian, K.; Kapelan, Z.; Mousavi, S. J.; Alani, A. Can smart rainwater harvesting schemes result in the improved performance of integrated urban water systems? *Environ. Sci. Pollut. Res.* **2018**, *25*, 19271-19282.
- Brand, M. W.; Gudiño-Elizondo, N.; Allaire, M.; Wright, S.; Matson, W.; Saksa, P.; Sanders, B. F. Stochastic Hydro-Financial Watershed Modeling for Environmental Impact Bonds. *Water Resour. Res.* **2020**, *56* (8), e2020WR027328.
- Brooks, K. N., Ffolliott, P. F., & Magner, J. A. (2013). *Hydrology and the Management of Watersheds* (4th Edition). Ames, IA: John Wiley & Sons, Inc.
- California State Water Resources Control Board. *Strategy to Optimize Resource Management of Storm Water (STORMS)*, **2016**, Sacramento, CA.
- Campisano, A.; Creaco, E.; Modica, C. Application of Real-Time Control Techniques to Reduce Water Volume Discharges from Quality-Oriented CSO Devices. *J. Environ. Eng.* **2016**, *142* (1), 04015049.
- Carpenter, J. F.; Vallet, B.; Pelletier, G.; Lessard, P. Vanrolleghem, P. A. Pollutant removal efficiency of a retrofitted stormwater detention pond. *Water Qual. Res. J. Can.* **2014**, *49* (2), 124-134.
- City of Alexandria, VA. *CSS Long Term Control Plan Update Alternatives, Alternatives Evaluation: Storage Tanks*. **2015**. Department of Transportation and Environmental Services, Alexandria, VA.
- DC Water. *2020 Annual Report*. District of Columbia Water and Sewer Authority, Washington, DC. **2020**. https://www.dewater.com/sites/default/files/documents/annual_report_2020.pdf

Eggiman, S.; Mutzner, L.; Wani, O.; Schneider, M. Y.; Spuhler, D.; de Vitry, M. M.; Beutler, P.; Maurer, M. The Potential of Knowing More: A Review of Data-Driven Urban Water Management. *Environ. Sci. Technol.* **2017**, *51* (5), 2538-2553.

Ewing, G.; Demir, I. An ethical decision-making framework with serious gaming: a smart water case study on flooding. *J. Hydroinform.* **2021**, jh2021097.

Federico, F.; Youngdahl, A.; Subramanian, S.; Rauser, C.; Gold, M. *2019 Sustainable LA Grand Challenge Environmental Report Card for Los Angeles County Water*. University of California, Los Angeles, **2019**, Los Angeles, CA.

Finewood, M. H.; Matsler, A. M.; Zivkovich, J. Green Infrastructure and the Hidden Politics of Urban Stormwater Governance in a Postindustrial City. *Ann. Am. Assoc. Geogr.* **2019**, *109* (3), 909-925.

Gaborit, E.; Anctil, F.; Pelletier, G.; Vanrolleghem, P. A. Exploring forecast-based management strategies for stormwater detention ponds. *Urban Water J.* **2016**, *13* (8), 841-851.

Gaborit, E.; Muschalla, D.; Vallet, B.; Vanrolleghem, P. A.; Anctil, F. Improving the performance of stormwater detention basins by real-time control using rainfall forecasts. *Urban Water J.* **2013**, *10* (4), 230-246.

Garofalo, G.; Giordano, A.; Piro, P.; Spezzano, G.; Vinci, A. A distributed real-time approach for mitigating CSO and flooding in urban drainage systems. *J. Network Comput. Appl.* **2017**, *78*, 30-42.

Gleick, P. H. Transitions to freshwater sustainability. *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115* (36), 8863-8871.

Goodman, E. P. Smart City Ethics: The Challenge to Democratic Governance. *Oxford Handbook of the Ethics of Artificial Intelligence*, **2020**. <http://dx.doi.org/10.2139/ssrn.3391388>

Grant, S. B.; Duong, K.; Rippey, M. A.; Pierce, G.; Feldman, D.; Zanetti, E.; McNulty, A. From yards to cities: a simple and generalizable probabilistic framework for upscaling outdoor water conservation behavior. *Environ. Res. Lett.* **2020**, *15*, 054010.

Grant, S.B.; Fletcher, T.D.; Feldman, D.; Saphores, J.-D.; Cook, P.L.M.; Stewardson, M.; Low, K.; Burry, K.; Hamilton, A.J. Adapting urban water systems to a changing climate: Lessons from the Millennium Drought in Southeast Australia. *Environ. Sci. Technol.* **2013** *47*, 10727-10734.

Grant, S. B.; Saphores, J.-D.; Feldman, D. L.; Hamilton, A. J.; Fletcher, T. D.; Cook, P. L. M.; Stewardson, M.; Sanders, B. F.; Levin, L. A.; Ambrose, R. F.; et al. Taking the “Waste” Out of “Wastewater” for Human Water Security and Ecosystem Sustainability. *Science* **2012**, *337* (6095), 681–686.

Grebel, J. E.; Mohanty, S. K.; Torkelson, A. A.; Boehm, A. B.; Higgins, C. P.; Maxwell, R. M.; Nelson, K. L.; Sedlak, D. L. Engineered Infiltration Systems for Urban Stormwater Reclamation. *Environ. Eng. Sci.* **2013**, *30* (8), 437–454.

Harris, I.; Jones, P. D.; Osborn, T. J.; Lister, D. H. Updated high-resolution grids of monthly climatic observations – the CRU TS3.10 Dataset. *Int. J. Clim.* **2014**, *34* (3), 623–642.

Han, M. Y.; Mun, J. S. Operational data of the Star City rainwater harvesting system and its role as a climate change adaptation and a social influence. *Water Sci. Technol.* **2011**, *63* (12), 2796–2801.

Hererra, D.; Cunniff, S.; DuPont, C.; Cohen, B.; Gangi, D.; Kar, D.; Snider, N. P.; Rojas, V.; Wyerman, J.; Norriss, J.; Mountenot, M. Designing an environmental impact bond for wetland restoration in Louisiana. *Ecosyst. Serv.* **2019**, *35*, 260–276.

Hill, D.; Kerkez, B.; Rasekh, A.; Ostfeld, A.; Minsker, B.; Banks, M. K. Sensing and Cyberinfrastructure for Smarter Water Management: The Promise and Challenge of Ubiquity. *J. Water Resour. Plann. Manage.* **2014**, *140* (7), 01814002.

Hofer, T.; Montserrat, A.; Gruber, G.; Gamerith, V.; Corominas, L.; Muschalla, D. A robust and accurate surrogate method for monitoring the frequency and duration of combined sewer overflows. *Environ. Monit. Assess.* **2018**, *190*, 209.

Hopkins, K. G.; Grimm, N. B.; York, A. M. Influence of governance structure on green stormwater infrastructure investment. *Environ. Sci. Pol.* **2018**, *84*, 124–133.

Horne, A. C.; Kaur, S.; Szemis, J. M.; Costa, A. M.; Nathan, R.; Webb, J. A.; Stewardson, M. J.; Boland, N. Active Management of Environmental Water to Improve Ecological Outcomes. *J. Water Resour. Plann. Manage.* **2018**, *144* (12), 04018079.

Jacopin, C.; Lucas, E.; Desbordes, M.; Bourgoigne, P. Optimisation of operational management practices for the detention basins. *Water Sci. Technol.* **2001**, *44* (2–3), 277–285.

Kerkez, B.; Gruden, C.; Lewis, M.; Montestruque, L.; Quigley, M.; Wong, B.; Bedig, A.; Kertesz, R.; Braun, T.; Cadwalader, O.; Poresky, A.; Pak, C. Smarter Stormwater Systems. *Environ. Sci. Technol.* **2016**, *50* (14), 7267–7273.

Low, K. G.; Grant, S. B.; Hamilton, A. J.; Gan, K.; Saphores, J.-D.; Arora, M.; Feldman, D. L. Fighting Drought with Innovation: Melbourne’s Response to the Millennium Drought in Southeast Australia. *WIREs Water* **2015**, *2* (4), 215–328.

Lund, N. S. V.; Falk, A. K. V.; Borup, M.; Madsen, H.; Mikkelsen, P. S. Model predictive control of urban drainage systems: A review and perspective towards smart real-time water management. *Crit. Rev. Environ. Sci. Technol.* **2018**, *48* (3), 279–339.

- Luthy, R. G.; Wolfand, J. M.; Bradshaw, J. L. Urban Water Revolution: Sustainable Water Futures for California Cities. *J. Environ. Eng.* **2020**, *146* (7), 04020065.
- Madadgar, S.; AghaKouchak, A.; Farahmand, A.; Davis, S. J. Probabilistic estimates of drought impacts on agricultural production. *Geophys. Res. Lett.* **2017**, *44*, 7799-7807.
- Maiolo, M.; Palermo, S. A.; Brusco, A. C.; Pirouz, B.; Turco, M.; Vinci, A.; Spezzano, G.; Piro, P. On the Use of a Real-Time Control Approach for Urban Stormwater Management. *Water* **2020**, *12* (10), 2842.
- Martin, A. "A Pioneering Environmental Impact Bond for DC Water," Conservation Finance Network, **2017**. <https://www.conservationfinancenetwork.org/2017/01/02/pioneering-environmental-impact-bond-for-dc-water>
- Mazor, R. D.; May, J. T.; Sengupta, A.; McCune, K. S.; Bledsoe, B. P.; Stein, E. D. Tools for managing hydrologic alteration on a regional scale: Setting targets to protect stream health. *Freshw. Biol.* **2018**, *63* (8), 786-803.
- Mullapudi, A.; Bartos, M.; Wong, B.; Kerkez, B. Shaping Streamflow Using a Real-Time Stormwater Control Network. *Sensors* **2018**, *18* (7), 2259.
- Mullapudi, A.; Wong, B. P.; Kerkez, B. Emerging investigators series: building a theory for smart stormwater systems. *Environ. Sci.: Water Res. Technol.* **2017**, *3* (1), 66-77.
- Muschalla, D.; Vallet, B.; Ancil, F.; Lessard, P.; Pelletier, G.; Vanrolleghem, P. A. Ecohydraulic-driven real-time control of stormwater basins. *J. Hydrol.* **2014**, *511*, 82-91.
- NOAA National Centers for Environmental Information, Global Historical Climatology Network. <https://www.ncdc.noaa.gov/ghcn-daily-description>
- National Academies, Water Science and Technology Board, National Research Council. *Urban Stormwater Management in the United States*, The National Academies Press: Washington, DC, 2009.
- Parker, E. A.; Grant, S. B.; Cao, Y.; Rippy, M. A.; McGuire, K. J.; Holden, P. A.; Feraud, M.; Avasarala, S.; Liu, H.; Hung, W. C.; Rugh, M.; Jay, J.; Peng, J.; Shao, S.; Li, D. Predicting Solute Transport Through Green Stormwater Infrastructure with Unsteady Transit Time Distribution Theory. *Water Resour. Res.* **2021**, *57* (2), e2020WR028579.
- Pierce, G.; Gmoser-Daskalakis, K.; Jessup, K.; Grant, S. B.; Mehring, A.; Winfrey, B.; Rippy, M. A.; Feldman, D.; Holden, P.; Ambrose, R.; Levin, L. University Stormwater Management within Urban Environmental Regulatory Regimes: Barriers to Progressivity or Opportunities to Innovate? *Environ. Manage.* **2021**, *67*, 12-25.
- Pierce, G.; Gmoser-Daskalakis, K.; Rippy, M. A.; Holden, P. A.; Grant, S. B.; Feldman, D. L.; Ambrose, R. F. Environmental Attitudes and Knowledge: Do They Matter for Support and

Investment in Local Stormwater Infrastructure? *Soc. Nat. Resour.* **2021**, DOI: 10.1080/08941920.2021.1900963.

Pincetl, S.; Porse, E.; Mika, K. B.; Litvak, E.; Manago, K. F.; Hogue, T. S.; Gillespie, T.; Pataki, D. E.; Gold, M. Adapting Urban Water Systems to Manage Scarcity in the 21st Century: The Case of Los Angeles. *Environ. Manage.* **2019**, *63*, 293-308.

Porse, E.; Mika, K. B.; Litvak, E.; Manago, K. F.; Hogue, T. S.; Gold, M.; Pataki, D. E.; Pincetl, S. The economic value of local water supplies in Los Angeles. *Nat. Sustain.* **2018**, *1*, 289-297.

Rajah, K.; O'Leary, T.; Turner, A.; Petrakis, G.; Leonard, M.; Westra, S. Changes to the temporal distribution of daily precipitation. *Geophys. Res. Lett.* **2014**, *41*, 8887-8894.

Ramsey, E.; Pesantez, J.; Fasaee, M. A. K.; DiCarlo, M.; Monroe, J.; Berglund, E. Z. A Smart Water Grid for Micro-Trading Rainwater: Hydraulic Feasibility Analysis. *Water* **2020**, *12* (11), 3075.

Reeves, R.L.; Grant, S.B.; Mrse, R.D.; Oancea, C.M.C.; Sanders, B.F.; Boehm, A.B. Scaling and management of fecal indicator bacteria in runoff from a coastal urban watershed in Southern California. *Environ. Sci. Technol.* **2004**, *38* (9), 2637-2648.

Roman, D.; Braga, A.; Shetty, N.; Culligan, P. Design and Modeling of an Adaptively Controlled Rainwater Harvesting System. *Water* **2017**, *9* (12), 974.

Sadegh, M.; Ragno, E.; AghaKouchak, A. Multivariate Copula Analysis Toolbox (MvCAT): Describing dependence and underlying uncertainty using a Bayesian framework. *Water Resour. Res.* **2017**, *53*, doi:10.1002/2016WR020242.

Schell, C. J.; Dyson, K.; Fuentes, T. L.; Des Roches, S.; Harris, N. C.; Miller, D. S.; Woelfle-Erskine, C. A.; Lambert, M. R. The ecological and evolutionary consequences of systemic racism in urban environments. *Science*. **2020**, *369*, eaay4497.

Stein, E. D.; Sengupta, A.; Mazor, R. D.; McCune, K.; Bledsoe, B. P.; Adams, S. Application of regional flow-ecology relationships to inform watershed management decisions: Application of the ELOHA framework in the San Diego River watershed, California, USA. *Ecohydrology* **2017**, *10* (7), e1869.

Swain, D. L.; Langenbrunner, B.; Neelin, J. D.; Hall, A. Increasing precipitation volatility in twenty-first century California. *Nat. Clim. Change* **2018**, *8*, 427-433.

Taguchi, V. J.; Weiss, P. T.; Gulliver, J. S.; Klein, M. R.; Hozalski, R. M.; Baker, L. A.; Finlay, J. C.; Keeler, B. L.; Nieber, J. L. It Is Not Easy Being Green: Recognizing Unintended Consequences of Green Stormwater Infrastructure. *Water* **2020**, *12* (2), 522.

UC Irvine. *University of California, Irvine Water Action Plan*. 2017. Irvine, CA.

US EPA Region 9. Total Maximum Daily Loads for Toxic Pollutants, San Diego Creek and Newport Bay, CA, Technical Support Document Part B. US EPA, 2002.

US EPA. *Results of the Nationwide Urban Runoff Program*. Water Planning Division, PB 84-185552. EPA: Washington, DC, 1983.

US EPA. *Smart Data Infrastructure for Wet Weather Control and Decision Support*. Office of Wastewater Management, 830-B-17-004. EPA: Washington, DC, 2018.

Vinuesa, R.; Azizpour, H.; Leite, I.; Balaam, M.; Dignum, V.; Domisch, S.; Fellander, A.; Langhans, S. D.; Tegmark, M.; Nerini, F. F. The role of artificial intelligence in achieving the Sustainable Development Goals. *Nat. Commun.* **2020**, *11*, 233.

Walsh, C. J.; Roy, A. H.; Feminella, J. W.; Cottingham, P. D.; Groffman, P. M.; Morgan, R. P. The urban stream syndrome: current knowledge and the search for a cure. *J. North Am. Benthol. Soc.* **2005**, *24*, 706–723.

Wu, H.; Huang, G.; Meng, Q.; Zhang, M.; Li, L. Deep Tunnel for Regulating Combined Sewer Overflow Pollution and Flood Disaster: A Case Study in Guangzhou City, China. *Water* **2016**, *8* (8), 329.

Xu, W. D.; Burns, M. J.; Cherqui, F.; Fletcher, T. D. Enhancing stormwater control measures using real-time control technology: a review. *Urb. Water J.* **2021**, *18* (2), 101-114.

Xu, W. D.; Fletcher, T. D.; Burns, M. J.; Cherqui, F. Real Time Control of Rainwater Harvesting Systems: The Benefits of Increasing Rainfall Forecast Window. *Water Resour. Res.* **2020**, *56*, e2020WR027856.

Xu, W. D.; Fletcher, T. D.; Duncan, H. P.; Bergmann, D. J.; Breman, J.; Burns, M. J. Improving the Multi-Objective Performance of Rainwater Harvesting Systems Using Real-Time Control Technology. *Water* **2018**, *10* (2), 147.

Appendix A

Supporting Information for Chapter 2

Introduction

This Supporting Information includes detailed methods for conducting the 2015/2016 experiments, followed by a detailed description of calculating theoretical single collector contact efficiencies. We have also included tables summarizing (1) porosity and dispersivity estimates, (2) the candidate regression models for explaining variability in FIB removal rates, and (3) additional characteristics of the biofilter sites mentioned in the main text. References are summarized at the end.

Detailed Methods for 2015/2016 FIB Experiment and Salt Pulse Experiment

General Protocol for Experiments

Pulses of either secondary-treated sewage (for the FIB experiment) or a NaCl or NaBr (salt) solution (for the salt pulse experiment) were applied to the biofilters under fully saturated and constant pressure head conditions. Constant flow was achieved by maintaining a constant pressure head difference across the top and bottom of the biofilter with an overflow drain installed in the ponding zone (~5 cm above the fine sand layer) and a bottom outlet (elevated ~0.4 m above the base of the biofilter). Because the salt pulse might adversely affect *Carex* and/or the microbial community in the biofilter, we carried out the FIB pulse experiment before the salt pulse experiment in 2015. In 2016, we switched to NaBr as the conservative tracer, which allowed us to use a lower salt concentration (200 mg Br⁻ L⁻¹) and avoid the issue of high salt levels potentially affecting the biofilter flora and fauna. Biofilters were saturated 24 hours prior to pulse experiments by continuously adding tap water to the ponding zone and thus maintaining a constant head at the top of the biofilter. The following protocol was adopted to minimize dilution of the secondary-treated sewage and salt pulses. At the start of each pulse, the supply of tap water was turned off and water in the ponding zone was allowed to drain until level with the top of the fine sand layer. At this point, each pulse (~1 L) was poured from its initial container into a plastic container, the bottom of which was perforated with small holes. The pulse was poured in while the plastic container was held 10 cm above the biofilter, so that its contents were gently “sprinkled” on the biofilter surface at a constant flow rate. After the pulse was deposited on the biofilter surface, both the initial pulse container and the perforated container were rinsed with deionized water above the biofilter surface to ensure that the entire pulse volume entered the biofilter and was not retained in the containers. The pulse was allowed to drain until the water was again level with the top of the fine sand layer. The tap water was then turned back on, whereupon the constant pressure head at the top of the fine sand layer was restored and maintained for the duration of the experiment. The volumetric flow rate was monitored (by manually recording the time required for outflow from the biofilter to fill a 1 L graduated cylinder) every hour during both the secondary-treated sewage and salt pulse experiments. Measured volumetric flow rates (Q) were divided by biofilter cross-sectional area (A) to obtain measured infiltration rates ($I = Q/A$). Following the addition of the salt pulse, water samples were collected from the biofilter outlet for four hours at a sampling frequency

ranging from 0.067 to 1 min⁻¹, and then analyzed for conductivity (NaCl) or bromide concentration (NaBr) as described in the main text. Following the addition of the sewage pulse, water samples were collected from the biofilter outlet for three hours at a sampling frequency ranging from 0.05 to 0.5 min⁻¹, stored on ice, and then analyzed for FIB within six hours of collection. The secondary-treated sewage was collected one week prior to the start of the experiments and stored in a refrigerator (at 4° C) until used. FIB concentrations in the secondary sewage were measured immediately prior to each pulse (after approximately one week of storage in the refrigerator).

Calculating Theoretical Single Collector Contact Efficiencies

The single collector contact efficiency can be estimated from the following expression:¹

$$\eta_0 = 2.4 A_s^{1/3} \left(\frac{d_b}{d_c} \right)^{-0.081} \left(\frac{I d_c}{D_m} \right)^{-0.715} \left(\frac{H}{k_B T} \right)^{0.052} + 0.55 A_s \left(\frac{d_b}{d_c} \right)^{1.675} \left(\frac{H}{3\pi\mu d_b^2 I} \right)^{0.125} + 0.22 \left(\frac{d_b}{d_c} \right)^{-0.24} \left(\frac{d_b^2 (\rho_b - \rho_f) g}{18\mu I} \right)^{1.11} \left(\frac{H}{k_B T} \right)^{0.053} \quad (S1)$$

Variables appearing in equation (S1) represent the diameter (d_b), density (ρ_b), and molecular diffusion coefficient (D_m) of the FIB; the temperature (T), dynamic viscosity (μ), and density (ρ_f) of the interstitial fluid; and the gravitational constant (g), Hamaker constant (H), Boltzmann constant (k_B), infiltration rate (I) of water flowing through the filter, and the Happel Cell parameter (A_s) which is calculated as follows: $A_s = 2(1-w^5) / (2-3w+3w^5-2w^6)$ where $w = (1-\theta)^{1/3}$ and θ is porosity.

To estimate theoretical single collector contact efficiencies we assumed: (1) physical constants appropriate for our experiment conditions ($T = 292^\circ \text{K}$, $\mu = 1.2 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$, $\rho_f = 1000 \text{ kg m}^{-3}$, $g = 9.81 \text{ m s}^{-2}$, $H = 6.5 \times 10^{-21} \text{ kg m}^2 \text{ s}^{-2}$, $k_B = 1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$);² (2) FIB diameter^{3,4} ($d_b = 1 \times 10^{-6} \text{ m}$), density^{5,6} ($\rho_b = 1100 \text{ kg m}^{-3}$), and molecular diffusion coefficient estimated from the Stokes-Einstein equation¹ ($D_m = 3.6 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$) (*E. coli* and enterococci bacteria have similar diameters and densities); (3) the average filter media grain diameter ($d_c = 9.3 \times 10^{-4}$, calculated from the median grain size of each filter media layer weighted by the corresponding thickness of each layer); (4) porosity of $\theta = 0.4$ (the average porosity estimated from the salt pulse experiments, described in main text; see Table S1); and (5) infiltration rates consistent with the range of infiltration rates in the biofilter experiments ($I = 7 \times 10^{-6}$ to 2×10^{-4}).

Table S1. Porosity and dispersivity estimates from salt pulse experiments (with 95% credibility intervals in parentheses).

Biofilter	Porosity (unitless)	Dispersivity (m) $\times 10^{-2}$
Unplanted 1 (2015)	0.373 (0.371, 0.376)	0.972 (0.888, 1.07)
Unplanted 2 (2015)	0.379 (0.376, 0.382)	1.28 (1.19, 1.38)
Unplanted 3 (2015)	0.372 (0.369, 0.375)	1.33 (1.25, 1.44)
Unplanted 1 (2016)	0.400 (0.398, 0.401)	0.974 (0.931, 1.02)
Unplanted 2 (2016)	0.417 (0.416, 0.418)	0.678 (0.658, 0.698)
Unplanted 3 (2016)	0.417 (0.415, 0.418)	0.490 (0.466, 0.516)
Overall unplanted average (standard deviation)	0.393 (0.0210)	0.954 (0.329)
Planted 1 (2015)	0.321 (0.310, 0.331)	6.52 (5.85, 7.41)
Planted 2 (2015)	0.359 (0.340, 0.378)	6.07 (5.15, 7.42)
Planted 3 (2015)	0.350 (0.342, 0.358)	3.81 (3.45, 4.27)
Planted 1 (2016)	0.429 (0.425, 0.433)	0.845 (0.753, 0.965)
Planted 2 (2016)	0.429 (0.417, 0.441)	2.69 (2.32, 3.21)
Planted 3 (2016)	0.400 (0.392, 0.408)	2.71 (2.43, 3.07)
Overall planted average (standard deviation)	0.381 (0.0449)	3.78 (2.18)

Table S2: Candidate Regression Models Explaining Variability in FIB Removal Rates (k_{OBS})

MODELS	Parameters	Coefficients (SE) ¹	LMG ²	BIC ³	w_{BIC} ⁴	RMSE (LOOCV) ⁵	RMSE (tot) ⁶	R ² (tot) ⁷
Total Model: Data from 2015/2016 experiments and Chandrasena et al., experiments								
Model 1 (best-fit)	Intercept*	5.67 (0.753)	--					
	$\log 10(k_{\text{CBFT}})^*$	2.74 (0.216)	0.306					
	Antecedent dry period (days)*	-0.041 (0.004)	0.143	-89.8	0.686	0.135	0.181	0.658
	Column age (months)*	0.043 (0.005)	0.069					
	Shrub presence/absence*	-0.184 (0.050)	0.058					
	Study*	-0.255 (0.074)	0.081					
Partial Model: Data from Chandrasena et al., experiments only								
Model 1	Intercept*	10.8 (1.04)	--					
	$\log 10(k_{\text{CBFT}})^*$	4.17 (0.292)	0.392	-91.9	0.301	0.133	0.179	0.650
	Antecedent dry period (days)*	-0.043 (0.003)	0.187					
	Column age (months)*	0.016 (0.007)	0.071					
Model 2	Intercept*	12.2 (0.878)	--					
	$\log 10(k_{\text{CBFT}})^*$	4.52 (0.255)	0.477	-91.5	0.248	0.135	0.182	0.640
	Antecedent dry period (days)*	-0.040 (0.003)	0.163					
	Intercept*	9.94 (1.16)	--					
Model 3 (best-fit)	$\log 10(k_{\text{CBFT}})^*$	3.92 (0.345)	0.345					
	Antecedent dry period (days)*	-0.042 (0.004)	0.176	-89.9	0.096	0.132	0.178	0.655
	Column age (months)*	0.021 (0.007)	0.080					
	Shrub presence/absence ⁹	-0.090 (0.053)	0.054					

*. significant at the $p < 0.05$ level; ⁹marginally significant at the $p < 0.10$ level

¹SE: Standard Error; ²LMG: the contribution of each parameter to overall R² (assessed using the averaging over ordering method LMG); ³BIC: Bayesian Information Criterion;

⁴ w_{BIC} : BIC weights; ⁵RMSE (LOOCV): The weighted average Root Mean Squared Error (model predictive ability) estimated using Leave One Out Cross Validation;

⁶RMSE (tot): Root Mean Squared Error (full model); ⁷R² (tot): Coefficient of Determination (full model)

Table S3. Selected biofilter site characteristics used in Figure 3.

Site Name	Biofilter Area (A) (m^2)	Catchment Area (A_c) (ha)	Catchment Ratio (CR) (%)
<i>Southern California</i>			
Elmer Avenue (multiple)	24	16	0.015
Irvine Caltrans	810	1.6	5.1
<i>Victoria, Australia</i>			
Hereford Road	100	0.9	1.1
Parker Street (multiple)	33	0.1	3.3

Biofilter and catchment areas were obtained from Ambrose and Winfrey et al. (2015).⁷

Appendix A References

- [1] Tufenkji, N.; Elimelech, M. Correlation Equation for Predicting Single-Collector Efficiency in Physicochemical Filtration in Saturated Porous Media. *Environ. Sci. Technol.* **2004**, *38* (2), 529–536.
- [2] Redman, J. A.; Walker, S. L.; Elimelech, M. Bacterial Adhesion and Transport in Porous Media: Role of the Secondary Energy Minimum. *Environ. Sci. Technol.* **2004**, *38* (6), 1777–1785.
- [3] Nelson, D. E.; Young, K. D. Penicillin Binding Protein 5 Affects Cell Diameter, Contour, and Morphology of *Escherichia coli*. *J. Bacteriol.* **2000**, *182* (6), 1714–1721.
- [4] Kokkinosa, A.; Fasseas, C.; Eliopoulos, E.; Kalantzopoulos, G. Cell size of various lactic acid bacteria as determined by scanning electron microscope and image analysis. *Le Lait* **1998**, *78* (5), 491–500.
- [5] Kubitschek, H. E.; Baldwin, W. W.; Graetzer, R. Buoyant density constancy during the cell cycle of *Escherichia coli*. *J. Bacteriol.* **1983**, *155* (3), 1027–1032.
- [6] Higgins, M. L.; Haines, M.; Whalen, M.; Glaser, D.; Bylund, J. Relationship between changes in buoyant density and formation of new sites of cell wall growth in cultures of streptococci (*Enterococcus hirae* ATCC 9790) undergoing a nutritional shift-up. *J. Bacteriol.* **1990**, *172* (8), 4415–4419.
- [7] Ambrose, R. F.; Winfrey, B. K. Comparison of stormwater biofiltration systems in Southeast Australia and Southern California. *WIREs Water* **2015**, *2*, 131–146.

Appendix B

Supporting Information for Chapter 3

Introduction

This Supporting Information includes a detailed description of how we estimated crop potential evapotranspiration (**Text S1**). Next, we describe our numerical evaluation of the biofilter bucket hydrology model (**Text S2**) and describe how we estimated saturated hydraulic conductivity (**Text S3**). We also provide detailed derivations (and illustrate their numerical application) for age-ranked storage under uniform selection (**Text S4**), the age structure of water in the biofilter (**Text S5**), and TTD theory predictions for solute transport (**Text S6**). We then describe how the fraction of inflow that undergoes lateral exfiltration was estimated using both steady-state and transient experiments (**Text S7**). We describe how we corrected experimental timestamps so that the modeled and measured outflow volumes and concentrations aligned (**Text S8**), and document key differences between the experimental storms carried out during the summer of 2018 and 2019 (**Text S9**). **Table S1** summarizes water volume recovery and bromide mass recovery for storm simulation experiments in 2018 and 2019. References are summarized at the end.

Text S1. Estimating Crop Potential Evapotranspiration (cPET)

Crop Potential Evapotranspiration (cPET) was estimated outside of Hydrus using the Penman-Monteith equation (Allen et al., 1998; FAO-56):

$$pET = \frac{1}{\lambda \rho_w} \frac{\Delta(R_n - G) + \rho_a c_p \frac{(e_s - e_a)}{r_a}}{\Delta + \gamma \left(1 + \frac{r_s}{r_a}\right)} \quad (1-1)$$

Here, R_n = net radiation (calculated, not measured, as a function of albedo, latitude and longitude, and climate variables; average temperature, relative humidity, and solar radiation), r_s = surface resistance (a function of stomatal conductance, and the leaf area index; LAI), r_a = atmospheric resistance (a function of plant height, wind speed, and the height at which wind speed and relative humidity measurements were made), G = the soil heat flux (a function of solar radiation and R_n), $e_s - e_a$ = the pressure deficit of the air (a function of temperature and relative humidity), Δ = the slope of the saturation vapor pressure temperature relationship, ρ_a = the mean air density at the elevation of the biofilter, ρ_w = the mean water density at constant pressure, c_p = the specific heat of air, γ = the psychrometric constant, and λ = the latent heat of water. Each of the above-noted parameters was estimated, using the procedure described in Allen et al. (1998), at an hourly time step over the two time periods (June 25-29 in 2018, and June 1-5 in 2019) when biofilter challenge experiments were conducted at the Orange County Public Works LID Campus, City of Orange, Orange County, California. Data resources included the following. Temperature and wind speed data (sensor height: 3.7 m; back adjusted to 2 m as per Allen et al., 1998) were sourced from the onsite weather station at Orange County Public Works. Solar radiation, and relative humidity data were sourced from CIMIS station 75 located ~ 19.34 km SE of Orange County Public Works. Plant trait information appropriate for *Carex sp* was used in lieu of standard FAO values for a well-watered turf grass, and included the following. Maximum stomatal conductance was set to 0.45 mol H₂O/m²/s based on measured values for *Carex hirta*, a *Carex* species capable of tolerating the range of dry and wet soil conditions typical of stormwater biofilters (Busch & Losch, 1998). LAI was set to 1.265, an average value from four *Carex* species evaluated by Aerts et al., 1992 (min LAI: 0.75, max LAI: 2.49). Plant height was set to 0.41m, the average height of *Carex* plants in the 2019 biofilter experiments. The standard FAO value for albedo (0.23) was used as *Carex*-specific estimates for albedo were unavailable (Allen et al., 1998).

Text S2. Numerical Solution of the Biofilter Bucket Hydrology Model. Figure S1 summarizes the process we used for the Hydrus 1D and bucket model water balance calculations. To numerically integrate the bucket hydrology model over the 17 experimental storms carried out during the summers of 2018 and 2019, we substituted the closure relationships for infiltration, discharge, and ET into the volume balance equation (equation (1a) in the main text):

$$\frac{dS(t)}{dt} = \begin{cases} I(t), & 0 < S(t) < S_{\max} \\ K_{\text{sat}}, & S(t) = S_{\max} \end{cases} - K_{\text{sat}} \left(\frac{S(t) - S_{\min}}{S_{\max}} \right)^g - c \text{PET}(t), \quad 0 \leq S(t) \leq S_{\max} \quad (2-1a)$$

$$S(t=0) = S_0 \quad (2-1b)$$

Terms on the righthand side were determined as follows:

- Inflow to the ponding zone, $I(t)$, was measured based on the change in weight of the inflow tank (Section 3.1, main text);
- The maximum storage, $S_{\max} = 0.246$ m, was calculated from the depth and porosity of the experimental biofilter, or inferred by minimizing the root mean square error between model predicted and measured bromide concentrations (Section 4.4, main text);
- The saturated hydraulic conductivity, K_{sat} , was determined from in situ measurements and measurements of peak outflow (Text S3);
- The gravitational discharge parameters, $S_{\min} = 0$ m and $g = 5.0$, were estimated by calibrating Kirchner's recession streamflow model to Hydrus 1D simulations (Section 4.2, main text).
- cPET was estimated from local environmental measurements using FAO guidelines (Text S1).
- Finally, the initial storage, $S_0 = 0.054$ m, is equal to Hydrus 1D default values for the field capacity of loamy sand (assuming a depth and porosity of $d_b = 0.6$ m and $\theta_s = 0.41$).

Numerical integration of equation (2-1a) was carried out using the NDSolve command in Mathematica as follows (in this particular implementation there are two saturated hydraulic conductivities: ksat1 (which applies from $t=0$ to $t=\text{tswitch}$) and ksat2 (which applies from $t=\text{tswitch}$ to $t=\text{tend}$), and sIC is the initial storage):

```
SVal[tend_, satIC0_, smax0_, g0_, ksat1_, ksat2_, tswitch0_] :=
Module[{t = tend, sIC = satIC0 smax0, smax = smax0, g = g0, kstart = ksat1, kend = ksat2, tswitch = tswitch0},
Print[smax, " ", " ", sIC];
NDSolve[{s'[u] == (1 - a[u]) (inflowinterp[u] - etinterp[u] - (ksat[u] (s[u] / smax)^g)),
p'[u] == a[u] (inflowinterp[u] - ksat[u]), q[u] == (ksat[u] (s[u] / smax)^g), ksat[0] == kstart,
q[0] == 0, a[0] == 0, p[0] == 0, s[0] == sIC, WhenEvent[s[u] > smax, a[u] -> 1],
WhenEvent[u > tswitch, {ksat[u] -> kend}], WhenEvent[p[u] < 0, {a[u] -> 0, p[u] -> 0}]},
{a, s, p, q, ksat}, {u, 0, t}, DiscreteVariables -> {a, ksat}]
```

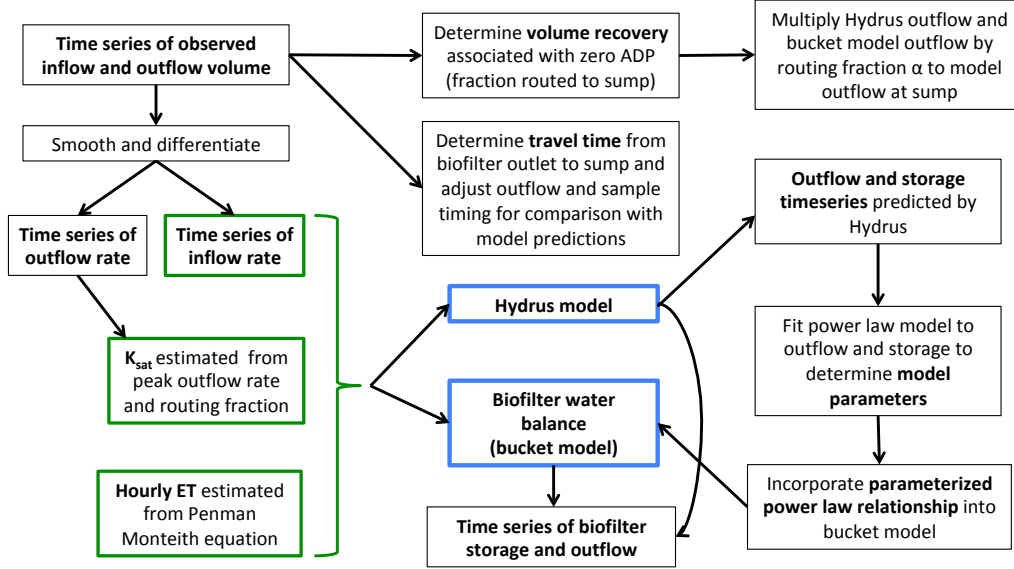


Figure S1. Flow diagram of key steps to estimate parameters used in the water balance calculations. Blue boxes indicate the two models used for estimating biofilter storage and outflow. Green boxes indicate the three inputs necessary for either model. ADP is antecedent dry period, ET is evapotranspiration, and K_{sat} is saturated hydraulic conductivity.

Text S3. Estimating Saturated Hydraulic Conductivity from Measured Biofilter Outflow

During the set of experiments conducted during the summer of 2018, peak flow rates measured at the outflow tank systematically declined from approximately 0.11 m h^{-1} (first two storms) to 0.09 m h^{-1} (next four storms) to 0.08 m h^{-1} (final four storms). For the set of experiments conducted in 2019, the peak flow rates declined from approximately 0.12 m h^{-1} (first two storms) to 0.08 m h^{-1} (final five storms). Accounting for the fraction of water recovered in 2018 and 2019 ($\alpha = 0.46 \pm 0.04$) (see Text S7) the implied saturated hydraulic conductivity values (under the assumption that the maximum outflow is equal to the saturated hydraulic conductivity (Durner & Iden, 2011; Mallants et al., 1997)) are $K_{sat} = 0.24, 0.20, 0.17 \text{ m h}^{-1}$ (first two, next four, and final four storms in 2018) and $K_{sat} = 0.26$ and 0.17 m h^{-1} (first two and final five storms in 2019). These K_{sat} values are consistent with eleven in situ measurements carried out during the 2019 experiments with a Philip-Dunne Infiltrometer ($K_{sat} = 0.22 \pm 0.62 \text{ m h}^{-1}$) and in the range of Hydrus 1D's default value for loamy sand (0.146 m h^{-1}) (Hydrus 1D, Version 4.17.0140, PC-Progress, Prague, Czech Republic). The consistent decline in saturated hydraulic conductivity observed across the storm events simulated in the summers of 2008 and 2009 could be caused by one or more well-known processes that tend to reduce saturated hydraulic conductivity, including compaction caused by the repeated wetting and drying of sediments (c.f., Mapa et al., 1986) and the clogging of biofilter media by

suspended particles in the stormwater and sewage influent mixtures (Lindsey et al., 1992; Le Coustumer et al., 2012).

Text S4. Derivation and Implementation of TTD Theory Solutions Under Uniform Selection.

Derivation of the Solution for Age-Ranked Storage. Substituting the uniform SAS function into the conservation equation for age-ranked storage (equations (5b) and (4a), respectively, in the main text) we arrive at the governing partial differential equation to be solved where the superscript “U” denotes a uniform SAS function:

$$\frac{\partial S_T^U}{\partial t} = J(t) - (f_Q(t) + f_{ET}(t))S_T^U(T, t) - \frac{\partial S_T^U}{\partial T} \quad (4-1a)$$

$$f_Q(t) = \frac{Q(t)}{S(t)} \quad (4-1b)$$

$$f_{ET}(t) = \frac{ET(t)}{S(t)} \quad (4-1c)$$

$$S_T^U(T, t=0) = S_0 H(T - T_0) \quad (4-1d)$$

$$H(x) = \begin{cases} 0, & x < 0 \\ 1, & x > 0 \end{cases} \quad (4-1e)$$

$$S_T^U(T=0, t) = 0 \quad (4-1f)$$

The boundary condition (equation (4-1f)) ensures that no water volume stored in the biofilter has an age less than or equal to zero, $T=0$. For the initial condition, equation (4-1d), all of the volume of water initially in storage, S_0 [L], has a single age, $T=T_0$, where the function $H(x)$ (equation (4-1e)) is the Heaviside or step function. To solve the age conservation equation we begin by taking the Laplace transform of equations (4-1a) and (4-1d) with respect to the age variable, where $\tilde{S}_T$ is the Laplace image function of S_T , the independent variable p [T^{-1}] is the Laplace transform variable and the initial condition (equation (4-1f)) has been incorporated into equation (4-2a):

$$\frac{d\tilde{S}_T^U}{dp} = \frac{J(t)}{p} - (f_Q(t) + f_{ET}(t) + p)\tilde{S}_T^U(p, t) \quad (4-2a)$$

$$\tilde{S}_T^U(p, t=0) = S_0 \frac{e^{-pT_0}}{p} \quad (4-2b)$$

These last two equations can be readily integrated to yield an exact solution for age-ranked storage in the Laplace domain:

$$\tilde{S}_T^U(p, t) = e^{-\bar{f}_Q(t) - \bar{f}_{ET}(t)} \left[\frac{S_0 e^{-p(t+T_0)}}{p} + \int_0^t \frac{e^{-p(t-v)}}{p} e^{\bar{f}_Q(v) + \bar{f}_{ET}(v)} J(v) dv \right] \quad (4-3a)$$

$$\bar{f}_Q(t) = \int_0^t f_Q(u) du \quad (4-3b)$$

$$\bar{f}_{ET}(t) = \int_0^t f_{ET}(u) du \quad (4-3c)$$

The functions $\bar{f}_Q(x)$ and $\bar{f}_{ET}(x)$ represent the cumulative volume that left the biofilter by outflow and ET, respectively as of time t . Taking the inverse Laplace Transform of equation (4-3a) yields the following exact time-domain solution for age-ranked storage in the biofilter:

$$S_T^U(T, t) = e^{-\bar{f}_Q(t) - \bar{f}_{ET}(t)} \left[S_{fc} H(T - t - T_i) + \int_0^t H(T + v - t) e^{\bar{f}_Q(v) + \bar{f}_{ET}(v)} J(v) dv \right] \quad (4-4)$$

Numerical Implementation of the Exact Solution for Age-Ranked Storage. As a first step toward implementing this solution, the Heaviside function inside the integral term on the right hand side of equation (4-4) should be removed. Because the upper limit of the integral is greater than zero, $t > 0$, this integral can be rewritten as follows:

$$\int_0^t H(T + v - t) e^{\bar{f}_Q(v) + \bar{f}_{ET}(v)} J(v) dv = H(T - t) \int_0^t e^{\bar{f}_Q(v) + \bar{f}_{ET}(v)} J(v) dv + H(t - T) \int_{t-T}^t e^{\bar{f}_Q(v) + \bar{f}_{ET}(v)} J(v) dv$$

Substituting into equation (4-4) we arrive at the form of the age-ranked storage solution that appears in the main text (equation (6a)):

$$S_T^U(T, t) = e^{-\bar{f}_Q(t) - \bar{f}_{ET}(t)} \left[S_0 H(T - t - T_0) + \int_w^t e^{\bar{f}_Q(v) + \bar{f}_{ET}(v)} J(v) dv \right] \quad (4-5a)$$

$$w = \begin{cases} 0, & T - t > 0 \\ t - T, & T - t < 0 \end{cases} \quad (4-5b)$$

Evaluation of equation (4-5a) requires estimating the functions $\bar{f}_Q(t)$ and $\bar{f}_{ET}(t)$ (see equations (4-3b) and (4-3c)) and the integral term on the right hand side of equation (4-5a). We consider these in turn.

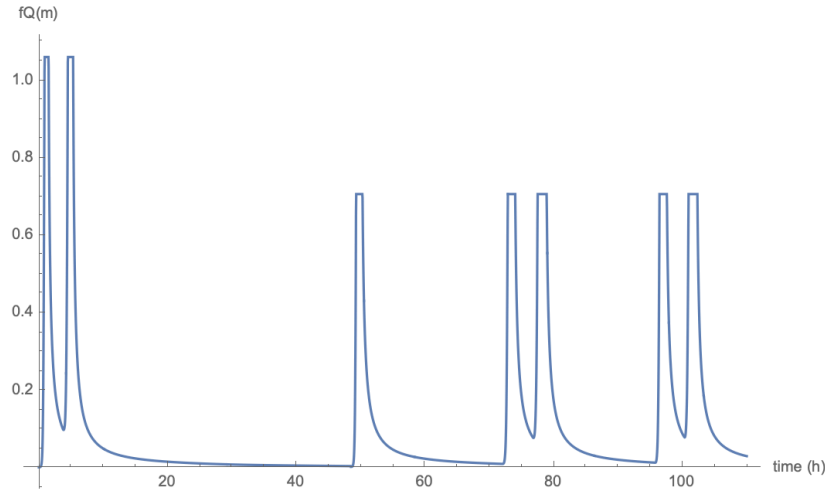


Figure S2. Bucket model predictions of the function, $f_Q(t) = Q(t)/S(t)$, for the sequence of seven storms simulated during the 2009 biofilter experiments.

As illustrated in Figure S2, the function, $f_Q(t)$, is highly oscillatory, taking on large values during storm events and approaching zero between storms. This oscillatory behavior implies that standard numerical algorithms for integrating $\bar{f}_Q(t)$ are slow to converge and prone to numerical error (results not shown). We resolved this problem by expressing the integral as a rate equation, which was then numerically integrating with the NDSolve command in Mathematica; e.g., the code below took 32 microseconds to evaluate.

```
Clear[fQbar, g];
soln = NDSolve[{g'[x] == fQ[x], g[0] == 0}, g, {x, 0, 110}, MaxStepFraction -> 0.0001];
fQbar[x_] := g[x] /. soln[[1]]

Timing[fQbar[110]]
{0.000032, 12.4892}
```

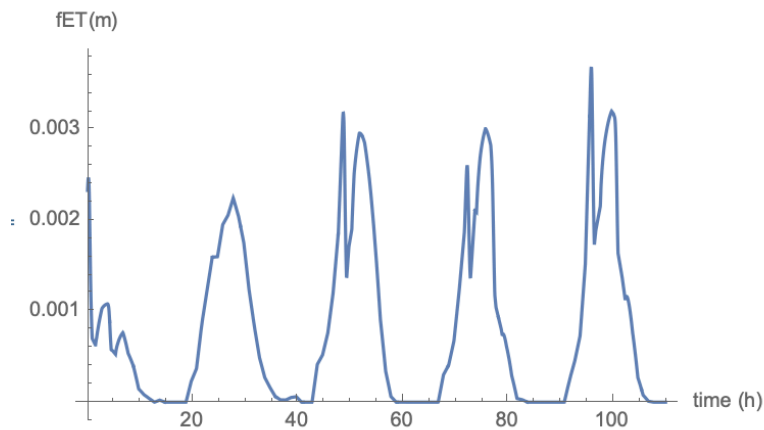


Figure S3. The oscillatory behavior of the function, $f_{ET}(t) = ET(t)/S(t)$, constructed from cPET estimates for our 2019 biofilter experiments (see Text S1), along with bucket model simulations of storage, $S(t)$.

Likewise, our 2019 time series for the function $f_{ET}(t)$ is highly oscillatory due to diurnal variation in solar radiation and hour-to-hour variations in vapor pressure deficit, cloud cover, and wind (Figure S3). We therefore evaluated the function, $\bar{f}_{ET}(t)$ (equation (4-3c)), using the same approach described above; namely, we expressed the integral as a rate equation which was numerically integrated with the NDSolve command in Mathematica; e.g., the Mathematica code illustrated below took 34 microseconds to evaluate.

```
Clear[fETbar, h];
soln2 = NDSolve[{h'[x] == fET[x], h[0] == 0}, h, {x, 0, 110}, MaxStepFraction -> 0.0001];
fETbar[x_] := h[x] /. soln2[[1]]

Timing[fETbar[110]]
{0.000034, 0.0927859}
```

Because infiltration is also highly oscillatory (taking on large positive values during storms, and equal to zero in the periods between storms) the integral term appearing on the right hand side of equation (4-5a) was evaluated using the same approach described above (i.e., expressing the integral as a rate equation and then integrating with the NDSolve command in Mathematica). The Mathematica code below took 88 ms to execute.

```
STIntegrationTerm[t_, T_] := Module[{soln, lowerlimit}, Clear[s, lowerlimit];
  If[t - T > 0, lowerlimit = t - T, lowerlimit = 0];
  STsoln = NDSolve[{s'[u] == Exp[-(fQbar[t] - fQbar[u]) - (fETbar[t] - fETbar[u])] j[u], s[lowerlimit] == 0},
    {s}, {u, lowerlimit, t}, MaxStepFraction -> 0.001]; s[t] /. STsoln[[1]]

Timing[STIntegrationTerm[110, 200]]
{0.088181, 0.112487}
```

The Mathematica code below was used to evaluate the overall solution for age-ranked storage:

```
stUniform[t_, T_, T0_, S0_] :=
  Module[{}, S0 HeavisideTheta[T - t - T0] Exp[-fQbar[t] - fETbar[t]] + STIntegrationTerm[t, T]]
```

Testing the Exact Solution for Age-Ranked Storage. It is easily verified that Equation (4-5a) satisfies the initial condition: $S_T^U(T, 0) = S_0 H(T - T_0)$. Next we demonstrate that this solution collapses to total storage when the water age, T , is set to a value larger than the oldest water in storage: $S_T^U(T \geq T_{oldest}, t) = S(t)$. At any time, t , the oldest water in the biofilter is the initial age of the original water in the biofilter (at time $t = 0$) plus the time that has elapsed since the start of the experiment: $T_{oldest} = T_0 + t$. The solution for age-

ranked storage was used to calculate the volume of water in the biofilter with age $T=51 \text{ h}+t$; i.e., one hour than the oldest water in the biofilter, assuming $T_0=50 \text{ h}$ (Figure S4).

```
Table[{t, stUniform[t, t + 51, 50, 0.054]}, {t, 0, 110, 1}];
```

```
ListPlot[%, AxesLabel → {"time (h)", "ST(m)"}]
```

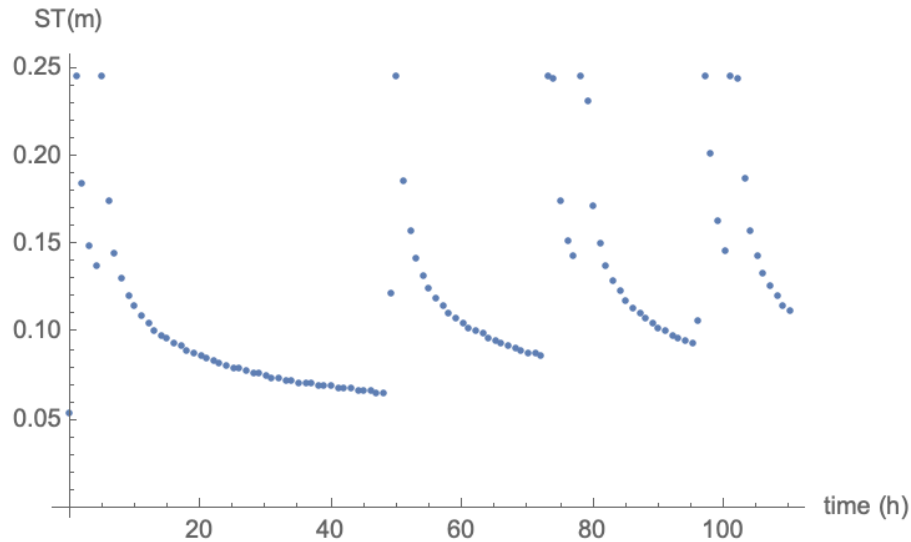


Figure S4. Values of age-ranked storage, predicted using equation (4-5a), for the choice of water age older than any water in storage, $T = 51 \text{ h} + t$, where the initial age is $T_0 = 50 \text{ h}$.

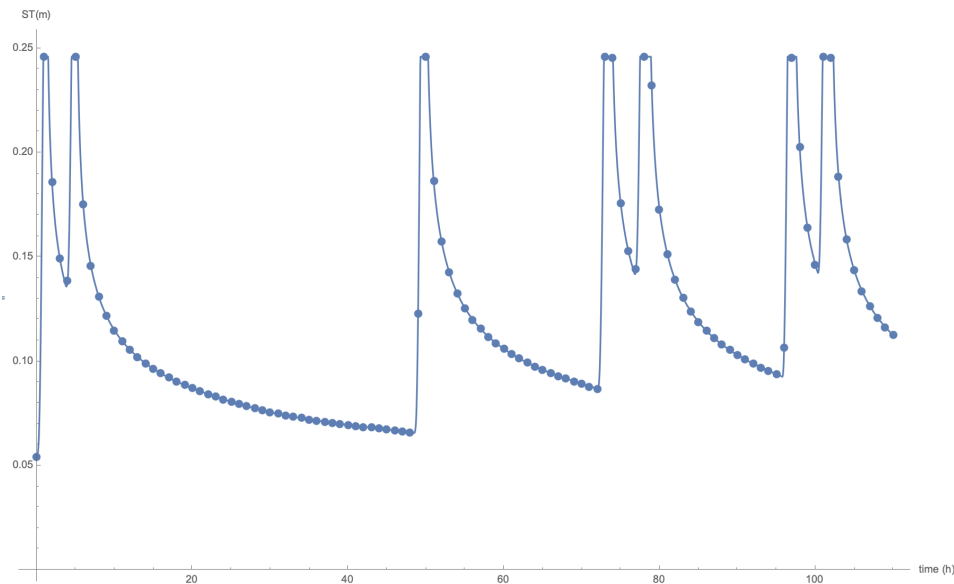


Figure S5. Comparison of the age-ranked storage values plotted in Figure S4 (points) with the total water volume in storage at any time ($S(t)$, solid line) determined from a bucket model unsteady water balance for the seven storms simulated during the 2019 experiments.

The age-ranked storage predictions align perfectly with the biofilter's time varying water volume (compare points and solid curve in Figure S5).

Text S5. Uniform Sampling Predictions for the Age Structure of Water in the Biofilter. The solution for age-ranked storage can be used to evaluate the contribution of individual storms to the evolving age distribution of water stored in the biofilter under uniform selection of the storage for the two outflows (discharge and ET). The residence time distribution (RTD) of stored water in the biofilter, at any time t , can be constructed by normalizing the age-ranked storage by the time varying volume of water in storage (see equation (4b) in the main text) (Harman, 2015):

$$P_{\text{RTD}}^U(T, t) = \frac{S_T^U(T, t)}{S(t)}$$

The corresponding probability density function (PDF) can be obtained by differentiating the CDF form of the RTD with respect to the age variable:

$$p_{\text{RTD}}^U(T, t) = \frac{\partial P_{\text{RTD}}^U}{\partial T} = \frac{1}{S(t)} \frac{\partial S_T^U}{\partial T} \quad (5-1)$$

Combining equations (4-5a) and (5-1) we arrive at the following expression for the PDF form of the biofilter storage RTD under uniform sampling:

$$p_{\text{RTD}}^U(T, t) = \frac{e^{-\bar{f}_Q(t) - \bar{f}_{\text{ET}}(t)}}{S(t)} \left[S_0 \delta(t + T_0 - T) + \frac{\partial}{\partial T} \int_w^t e^{\bar{f}_Q(v) + \bar{f}_{\text{ET}}(v)} J(v) dv \right]$$

Taking into consideration the two lower limits for w (see equation (4-5b)) and applying Leibnitz integration rule, the second term in the bracket can be simplified:

$$\frac{\partial}{\partial T} \int_a^t e^{\bar{f}_Q(v) + \bar{f}_{\text{ET}}(v)} J(v) dv = H(t - T) \frac{\partial}{\partial T} \int_{t-T}^t e^{\bar{f}_Q(v) + \bar{f}_{\text{ET}}(v)} J(v) dv = H(t - T) e^{\bar{f}_Q(t-T) + \bar{f}_{\text{ET}}(t-T)} J(t - T)$$

Thus, the PDF form of the biofilter's RTD can be written as follows (compare with equation (7b) in the main text):

$$p_{\text{RTD}}^U(T, t) = \delta(t + T_0 - T) \frac{S_0}{S(t)} e^{-\bar{f}_Q(t) - \bar{f}_{\text{ET}}(t)} + H(t - T) \frac{J(t - T)}{S(t)} e^{-\bar{f}_{\text{ET}}(t) + \bar{f}_{\text{ET}}(t-T) - \bar{f}_Q(t) + \bar{f}_Q(t-T)} \quad (5-2)$$

The first moment of equation (5-2) yields the expected value, or mean, of the age distribution for water in storage under uniform sampling:

$$\mu_{\text{RTD}}^U(t) = \int_0^\infty v p_{\text{RTD}}^U(v, t) dv \quad (5-3a)$$

$$\mu_{\text{RTD}}^U(t) = \left[\frac{S_0}{S(t)} e^{-\bar{f}_Q(t) - \bar{f}_{\text{ET}}(t)} \int_0^\infty T \delta(t + T_0 - T) dT + \int_0^\infty T H(t - T) \frac{J(t - T)}{S(t)} e^{-\bar{f}_{\text{ET}}(t) + \bar{f}_{\text{ET}}(t - T)} e^{-\bar{f}_Q(t) + \bar{f}_Q(t - T)} dT \right] \quad (5-3b)$$

The first integral on the righthand side of equation (5-3b) can be simplified after applying the combing property of the Dirac Delta function:

$$\int_0^\infty T \delta(t + T_0 - T) dT = t + T_0$$

Furthermore, the Heaviside function appearing in the second integral can be removed as follows:

$$\int_0^\infty T H(t - T) \frac{J(t - T)}{S(t)} e^{-\bar{f}_{\text{ET}}(t) + \bar{f}_{\text{ET}}(t - T)} e^{-\bar{f}_Q(t) + \bar{f}_Q(t - T)} dT = \frac{1}{S(t)} \int_0^t (t - u) J(u) e^{-\bar{f}_{\text{ET}}(t) + \bar{f}_{\text{ET}}(u)} e^{-\bar{f}_Q(t) + \bar{f}_Q(u)} du$$

Back substituting these results into equation (5-3b) we arrive at the final expression for the mean RTD under uniform storage selection (equation (7c) in the main text):

$$\mu_{\text{RTD}}^U(t) = \frac{1}{S(t)} \left[S_0 e^{-\bar{f}_Q(t) - \bar{f}_{\text{ET}}(t)} (t + T_0) + \int_0^t (t - u) J(u) e^{-\bar{f}_{\text{ET}}(t) + \bar{f}_{\text{ET}}(u)} e^{-\bar{f}_Q(t) + \bar{f}_Q(u)} du \right] \quad (5-3c)$$

Equation (5-3c) was numerically implemented by expressing the integral as a rate equation (see earlier) in Mathematica as follows:

```
Clear[MeanIntegral, q1, MeanIntegralSoln];
MeanIntegral[t_]:=
Module[{t = t0},
MeanIntegralSoln = NDSolve[{q1'[u] == (t - u) j[u] Exp[fQbar[u] - fQbar[t] + fETbar[u] - fETbar[t]], q1[0] == 0},
q1, {u, 0, t}, MaxStepFraction -> 0.0001];
q1[t] /. MeanIntegralSoln[[1]]]
meanRTD[t_, T0_, S0_] := (1/storage[t]) (S0 Exp[-fQbar[t] - fETbar[t]] (t + T0) + MeanIntegral[t])
```

Text S6. Uniform Selection Predictions for Solute Concentration in Gravitational Discharge

Our solution for age-ranked storage under uniform selection can also be used to calculate the concentration of a conservative solute in the biofilter outflow, $C_Q(t)$, by convolving the PDF form of the backward TTD with the concentration of solute, $C_j(t_i, T)$, that entered the biofilter at time, $t = t_i$, and left the biofilter as discharge at age T (Harman, 2015):

$$C_Q(t) = \int_0^t C_j(t - T, T) \bar{p}_Q(T, t) dT \quad (6-1)$$

Substituting equation (5-2) into equation (6-1) we arrive at the following solution for solute concentration in water discharged from the biofilter:

$$C_Q(t) = \int_0^t C_j(t - T) \delta(t + T_0 - T) \frac{S_0}{S(t)} e^{-\bar{f}_Q(t) - \bar{f}_{\text{ET}}(t)} dT + \int_0^t C_j(t - T) H(t - T) \frac{J(t - T)}{S(t)} e^{-\bar{f}_{\text{ET}}(t) + \bar{f}_{\text{ET}}(t - T)} e^{-\bar{f}_Q(t) + \bar{f}_Q(t - T)} dT$$

From the combining property of the Dirac Delta, and letting C_0 represent the solute concentration in “original water”, the first integral simplifies as follows:

$$\int_0^t C_J(t-T) \delta(t+T_0-T) \frac{S_0}{S(t)} e^{-\bar{f}_Q(t)-\bar{f}_{ET}(t)} dT = C_0 \frac{S_0 e^{-\bar{f}_Q(t)-\bar{f}_{ET}(t)}}{S(t)}$$

The Heaviside function appearing in the integrand of the second integral can be removed:

$$\frac{1}{S(t)} \int_0^t C_J(t-T) H(t-T) J(t-T) e^{-\bar{f}_{ET}(t)+\bar{f}_{ET}(t-T)} e^{-\bar{f}_Q(t)+\bar{f}_Q(t-T)} dT = \frac{1}{S(t)} \int_0^t C_J(t-T) J(t-T) e^{-\bar{f}_{ET}(t)+\bar{f}_{ET}(t-T)-\bar{f}_Q(t)+\bar{f}_Q(t-T)} dT$$

Thus, solute concentration discharged from the biofilter, assuming uniform sampling and no solute mass in the original water, becomes equal to equation (6-2) (compare with equation (8b) in the main text):

$$C_Q(t) = C_0 \frac{S_0 e^{-\bar{f}_Q(t)-\bar{f}_{ET}(t)}}{S(t)} + \frac{1}{S(t)} \int_0^t C_J(u) J(u) e^{-\bar{f}_{ET}(t)+\bar{f}_{ET}(u)-\bar{f}_Q(t)+\bar{f}_Q(u)} du \quad (6-2)$$

To tailor this equation to the 2018 and 2019 bromide pulse experiments, we can express the inflow concentration as follow, where $C_{J,m}$, $t_{m,s}$, and $t_{m,e}$ are the m -th storm's bromide concentration, start time and end time, respectively, and the sum is taken over all N storms where t_i is the entry time of a water parcel exiting the biofilter with gravitational discharge at time t :

$$C_J(t_i) = \sum_{m=1}^N C_{J,m} H(t_i - t_{m,s}) H(t_{m,e} - t_i) \quad (6-3)$$

Substituting equation (6-3) into equation (6-2), setting $C_0 = 0$ (reflecting the fact that there was no bromide present in the biofilter's original water during the field experiments), and using the distributive property of integration we obtain:

$$C_Q(t) = \frac{1}{S(t)} \sum_{m=1}^N C_{J,m} \int_0^t H(u - t_{m,s}) H(t_{m,e} - u) J(u) e^{-\bar{f}_{ET}(t)+\bar{f}_{ET}(u)-\bar{f}_Q(t)+\bar{f}_Q(u)} du \quad (6-4a)$$

The Heaviside functions inside the integral can be removed as follows:

$$\int_0^t H(u - t_{m,s}) H(t_{m,e} - u) J(u) e^{-\bar{f}_{ET}(t)+\bar{f}_{ET}(u)-\bar{f}_Q(t)+\bar{f}_Q(u)} du = \int_{t_{m,s}}^{t_{m,e}} J(u) e^{-\bar{f}_{ET}(t)+\bar{f}_{ET}(u)-\bar{f}_Q(t)+\bar{f}_Q(u)} du$$

Substituting this last result into equation (6-4a) we arrive at the following expression for the outflow concentration (compare with equations (9b) and (9c) in the main text):

$$C_Q(t) = \frac{1}{S(t)} \sum_{m=1}^N C_{J,m} H(t - t_{m,s}) \int_{t_{m,s}}^t J(u) e^{-\bar{f}_{ET}(t)+\bar{f}_{ET}(u)-\bar{f}_Q(t)+\bar{f}_Q(u)} du \quad (6-4b)$$

$$y = \begin{cases} t, & t < t_{m,e} \\ t_{m,e}, & t \geq t_{m,e} \end{cases} \quad (6-4c)$$

For example, during the 2019 experiments there was one storm that was spiked with bromide. Hence, in this case $N=1$ and our solution simplifies as follows, where the bromide addition occurred on the third storm, $m=3$:

$$C_Q(t) = H(t - t_{3,s}) \frac{C_{J3}}{S(t)} \int_{t_{3,s}}^y J(u) e^{-\bar{J}_{ET}(t) + \bar{J}_{ET}(u) - \bar{J}_Q(t) + \bar{J}_Q(u)} du \quad (6-5a)$$

$$y = \begin{cases} t, & t < t_{3,e} \\ t_{3,e}, & t \geq t_{3,e} \end{cases} \quad (6-5b)$$

The Mathematica code for implementing equation (6-5a) involves two steps; first numerically evaluating the integral and then evaluating the concentration in gravitational discharge from the biofilter at any time:

```
CQConc[t0_, k0_, ts_, te_, c0_] := Module[{t = t0, k = k0, lowerlimit = ts, upperlimit}, If[t < lowerlimit, Return[0]];
Clear[r];
If[t < te, upperlimit = t, upperlimit = te];
integralsoln = NDSolve[{r'[u] == Exp[-k t - fETbar[t] - fQbar[t] + k u + fETbar[u] + fQbar[u]] j[u], r[lowerlimit] == 0},
{r}, {u, lowerlimit, upperlimit}, MaxStepFraction -> 0.001];
c0 r[upperlimit] / storage[t] /. integralsoln[[1]]
```

Text S7. Experimental Approaches for Estimating Lateral Exfiltration from the Biofilter Test Cell

A summary of the process we used to estimate key parameters for the Hydrus 1D and bucket model water balance calculations is presented in Figure S1. One of the key parameters is the fraction of the inflow volume that is routed to the outflow tank. During the set of experimental storms simulated in the summers of 2018 and 2019 we measured time series of the inflow, $I(t)$ [$L T^{-1}$], to the biofilter and time series of the gravitational discharge from the biofilter routed to the outflow tank (see Figure 1c in the main text), $Q_{outflow}(t)$ [$L T^{-1}$]. We know from volume balance (accounting for the fact that ET was a negligible component of the biofilter's overall water balance, see Table S1) that not all inflow to the biofilter was routed to the outflow tank. We therefore let the fixed constant, α , represent the fraction of total gravitational discharge $Q(t)$ routed to the outflow tank: $Q_{outflow}(t) = \alpha Q(t)$. We determined α using two different approaches: (1) a steady-state experiment conducted during the summer of 2018; and (2) an analysis of the fraction of inflow volume recovered at the outflow tank for transient experimental storms simulated during the summers of 2018 and 2019. These two approaches are described next.

In the first approach, we conducted an experiment in July 2018 (using the same tank and scale experimental set-up described in Section 3.1 main text) in which we supplied a steady inflow of water to the ponding zone of the biofilter (10.1 L/min; the inflow tank was modified to maintain constant head) and simultaneously measured the outflow rate at the outflow tank. The outflow rate eventually stabilized at 5.6 L/min, implying a recovery of $\alpha = 0.55$.

The second approach involved, for each experimental storm in 2018 and 2019, calculating the total volume collected at the outflow tank and dividing it by the total volume of inflow delivered to the biofilter to obtain the storm's "volume recovery fraction". The volume recovery fraction values thus obtained increase inversely with antecedent dry period (ADP) ($R^2=0.82$, Figure S6), presumably because more of the inflow water went to increasing storage during storm events with longer ADPs. By this logic, extrapolating the fractional volume recovery back to an ADP of zero hours should yield the fraction of inflow routed to the outflow tank (under the assumption that none of the inflow water is going toward increasing storage when the ADP is zero). When this exercise is carried out for the set of storm experiments conducted during the summer of 2018 and 2019 we obtain a y-intercept of $\alpha = 0.46 \pm 0.04$ (Figure S6), which compares closely with the average volume recovery estimated during the steady-state experiments described above ($\alpha = 0.55$, see red horizontal line in Figure S6).

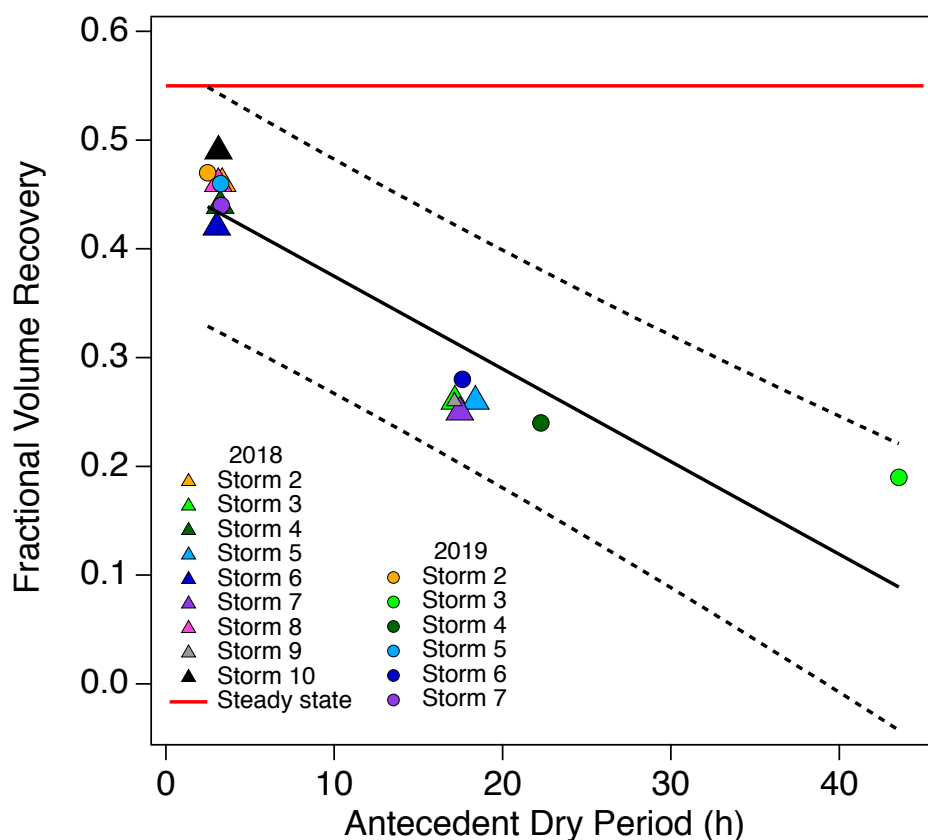


Figure S6. Fractional volume recovery and antecedent dry period (ADP) across 15 of the 2018 and 2019 storm experiments. Red line indicates the volume recovery during a steady-state experiment conducted in 2018. See Text S7 for details. Solid black line indicates best-fit line with 95% prediction intervals (dashed black lines). Storm 1 data from both years are not included in this analysis as the ADPs are not precisely known.

Text S8. Correcting the Time Stamps of Measured Outflow Rate and Bromide Breakthrough

Water leaving our biofilter through the underdrain had to flow by gravity down a manifold to an underground sump where it was pumped into the outflow tank (see Figure 1c in the main text). Our modeling framework was applied to a control volume that included the biofilter media. Consequently, in comparing model predictions measurements of volume and bromide concentration at the outflow tank, we needed to account for the time it takes water to transit from the biofilter underdrain to the outlet tank. We estimated this travel time experimentally by setting up a steady inflow of bromide-free water to the biofilter (using the constant head approach described in the last section). Once steady-state flow had been achieved we poured ~1L of bromide solution (NaBr dissolved in water) into the lateral connecting the biofilter's underdrain to the manifold. Water samples were collected at the outflow collection tank every minute for 14 minutes and measured for bromide concentration using an Orion bromide electrode (Thermo Fisher Scientific, Waltham, MA). From the bromide breakthrough curve, we estimated that the travel time from the biofilter underdrain to the outlet tank is about 3 – 12 minutes. As shown in Figure S7, our simplified infiltration model tended to over-estimate infiltration rates into the biofilter during the Filling Phase, and consequently the bucket model predictions for gravitational discharge tended to lead the gravitational discharge predicted by Hydrus 1D by about 15 minutes. Taking these two factors into account—the overly fast response of the bucket model's gravitational discharge predictions and the time delay associated with water transiting from the underdrain to the outflow tank—we adjusted timestamps of the measured outflow rate and bromide breakthrough curves backwards by 60 minutes. After time-adjustment, our measurements of flow and bromide concentration at the outflow tank aligned nearly perfectly with the Hydrus and age-conservation predictions of outflow rate and bromide concentration, respectively (see Figures 3 and 4 in the main text).

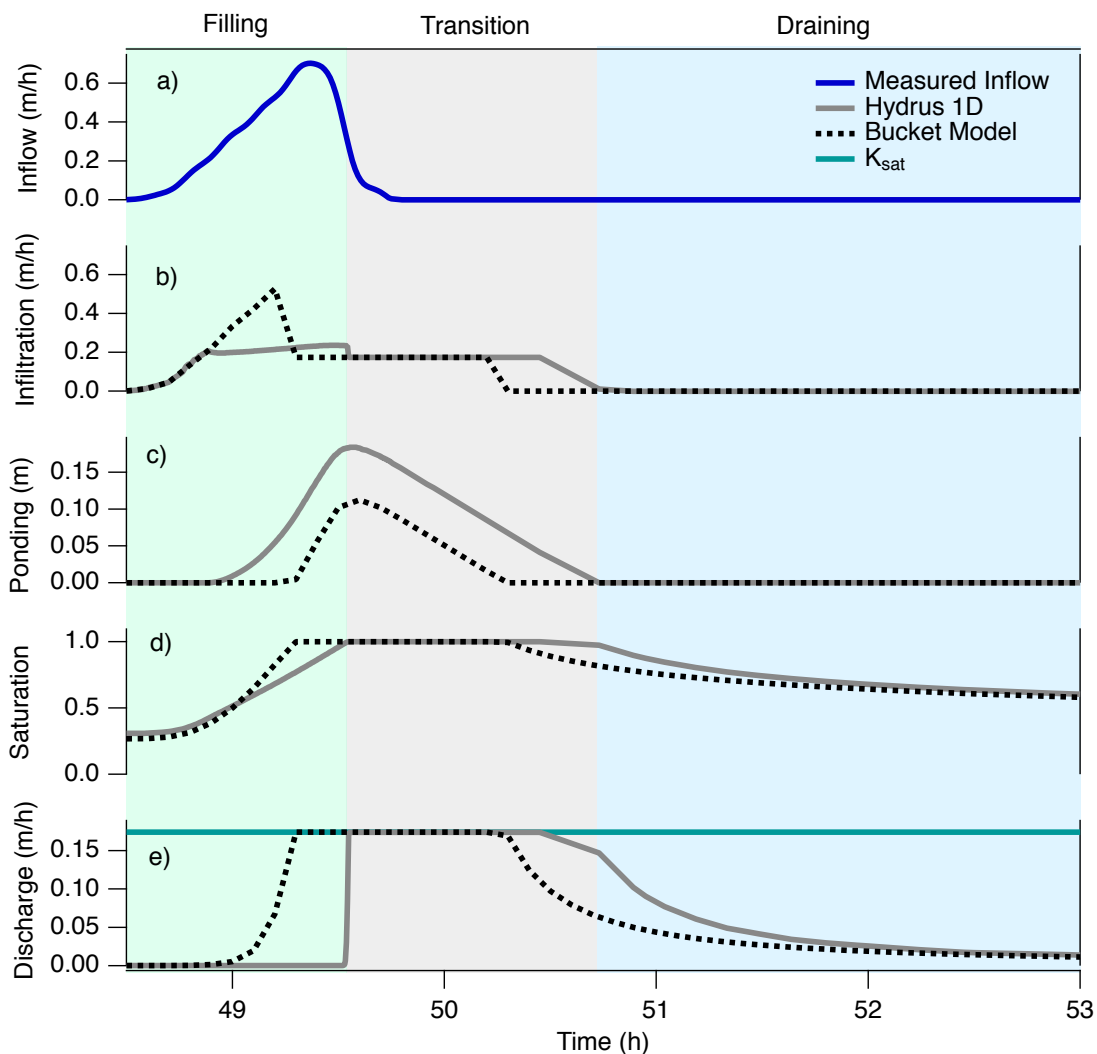


Figure S7. Measured inflow to the biofilter ponding zone (a), and Hydrus 1D and bucket model predictions of (b) surface infiltration, (c) ponding depth, (d) saturation, and (e) gravitational discharge for the third storm of the 2019 experiments. The three background panels designate the three phases described in Section 2.1.1 in the main text: Filling (light green), Transition (light gray), and Draining (light blue). Phase transitions are keyed to the Hydrus 1D simulations.

Text S9. Key Differences in the Experiments Conducted in the Summers of 2018 and 2019

Bromide tracer experiments conducted during the summers of 2018 and 2019 differed in several respects.

First, all of the 2018 storm events were carried out with tap water while, with one exception, all of the 2019 storm events were carried out with stormwater runoff from OCPW's LID campus that had been captured and stored in an 80,000 gallon underground cistern (StormCapture® System, Oldcastle Infrastructure, Inc., Atlanta, GA). The exception was the bromide-spiked third storm event in 2019, which

consisted of a 50:50 mixture of stormwater from the underground cistern and raw sewage from the local wastewater treatment plant (Orange County Sanitation District). The transition from tap water (in 2018) to stormwater (+/- sewage) (in 2019) was motivated by a desire to evaluate the removal of common stormwater contaminants (including heavy metals, nutrients, and microbial pathogens) under transient flow conditions, to be described in subsequent publications.

Second, averaged across all 2018 experimental storm events, ~ 50% of the water added to the biofilter was recovered at the outlet tank (see Text S7). As evapotranspiration (ET) was a relatively minor component of the overall water balance (<1%, see Table S1) we suspected that water was escaping the biofilter test cell into adjacent cells or the surrounding soil; i.e., exfiltration was occurring. Following the 2018 experiments and about five months prior to the 2019 experiments, we removed all plants from the biofilter, excavated the media and discovered that, when the test cell was originally constructed, the contractor had drilled a ca., 5 cm diameter hole into the base of the cinderblock wall separating our test cell from the adjacent cell to accommodate a buried irrigation water supply pipe. The hole was partially sealed (to the extent possible while leaving the irrigation supply pipe in place), the media was replaced, and the biofilter was replanted with a native sedge, *Carex spissa*, recommended for biofilters in southern California (County of San Diego, 2014).

Third, the operation of the control valve differed over the two years. In 2018, storms consisted of tap water and the discharge rate from the inflow tank through the control valve was continuously adjusted with a real-time control algorithm based on continuous measurements of water level in the inflow tank. This set-up could not be replicated in 2019, because the 50:50 mixture of stormwater and sewage applied during the third storm required vigorous mixing of the inflow tank, which interfered with the water level sensor. Consequently, during the 2019 experiments we operated the control valve manually, according to a schedule that roughly conformed to the design storm hydrograph. The storm hydrographs (estimated by differentiating the measured decline in weight of the inflow tank over time) generated using this approach compare reasonably well to the design storm, although the peak flow is reduced in both years, and the storm hydrographs in 2019 are smoother and more reproducible from storm-to-storm (Figure S8).

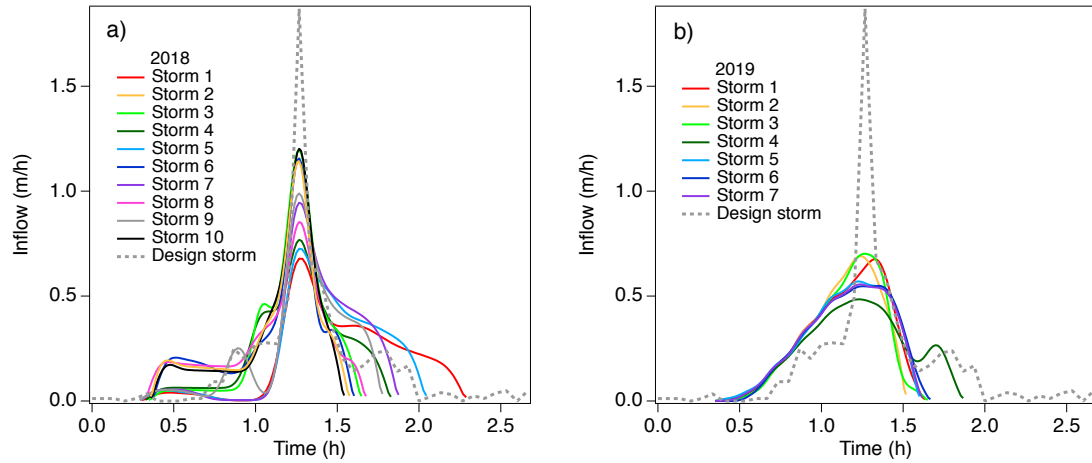


Figure S8. A comparison of the design storm (grey dashed curve) and measured inflow rates to the biofilter during the (a) 2018 and (b) 2019 experimental storms (colored curves).

Our inferred values of $s_{\max}$ (estimated by minimizing RMSE) were 0.73 m in 2018 and 0.42 m in 2019 (Figure S9).

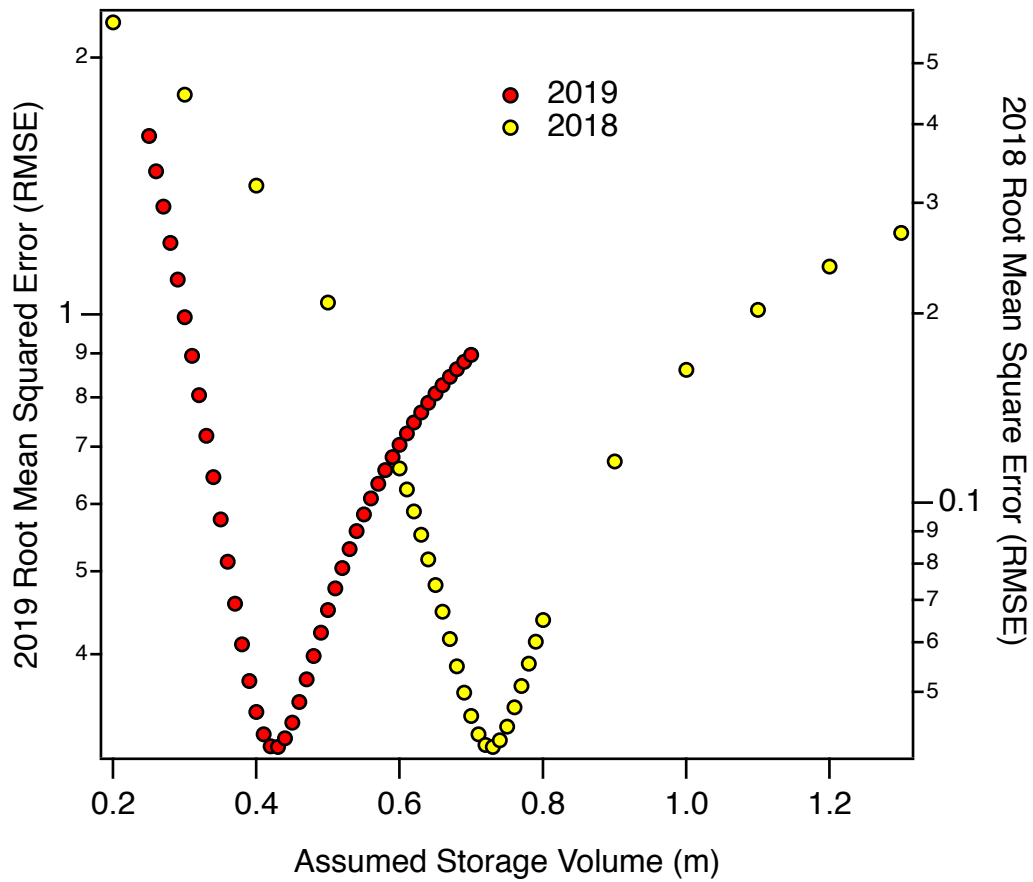


Figure S9. RMSE optimization of maximum storage for the 2018 and 2019 experiments.

Table S1. Total inflow volume delivered to the biofilter’s ponding zone, total volume recovered in the outflow tank, total ET (estimated by integrating the hourly cPET from the beginning of the storm to the beginning of the next storm (or in the case of 2018 Storm 10 and 2019 Storm 7, integrating hourly cPET over ten hours starting from the beginning of the storm)), and mass of bromide added and recovered for all storms simulated in 2018 and 2019. The inflow bromide mass column is marked not applicable (N/A) for storms that were not spiked with bromide, and the outflow bromide mass column is marked N/A for any storms that were conducted prior to the first bromide spiked storm of each year’s sequence.

	Inflow Volume (L)	Biofilter Area- normalized Inflow Volume (m)	Outflow Volume Recovered (L)	Biofilter Area- normalized Outflow Volume Recovered (m)	ET (m)	Mass of Br- in Inflow (g)	Mass of Br- Recovered in Outflow (g)	Cumulative Br- Mass Recovery (%)
2018 Storm 1	1540	0.414	435	0.117	0.00282	N/A	N/A	N/A
2018 Storm 2	1557	0.419	722	0.194	0.00167	75.8	15.9	21.0
2018 Storm 3	1540	0.414	413	0.111	0.00248	N/A	5.5	28.2
2018 Storm 4	1494	0.402	658	0.177	0.00254	72.9	19.5	27.5
2018 Storm 5	1546	0.416	399	0.107	0.00253	N/A	6.6	31.9
2018 Storm 6	1547	0.416	651	0.175	0.00206	76.3	18.7	29.4
2018 Storm 7	1535	0.413	378	0.102	0.00239	N/A	7.3	32.7
2018 Storm 8	1546	0.416	702	0.189	0.00199	74.7	19.7	31.1
2018 Storm 9	1553	0.418	410	0.110	0.00202	N/A	7.3	33.5
2018 Storm 10	1546	0.416	751	0.202	0.00200	68.6	19.4	32.6
2019 Storm 1	1433	0.386	302	0.0813	0.000581	N/A	N/A	N/A
2019 Storm 2	1376	0.370	649	0.175	0.00248	N/A	N/A	N/A
2019 Storm 3	1381	0.372	266	0.0716	0.00308	171.6	9.2	5.36
2019 Storm 4	1417	0.381	342	0.0920	0.00194	N/A	13.4	13.2
2019 Storm 5	1411	0.380	654	0.176	0.00127	N/A	12.2	20.3
2019 Storm 6	1392	0.375	397	0.107	0.00211	N/A	1.3	21.0
2019 Storm 7	1386	0.373	608	0.164	0.00142	N/A	0.8	21.5

Appendix B References

- Aerts, R., de Caluwe, H., & Konings, H. (1992). Seasonal allocation of biomass and nitrogen in four *Carex* species from mesotrophic and eutrophic fens as affected by nitrogen supply. *Journal of Ecology*, 80(4), 653-664.
- Allen, R. G., Pereira, L. S., Raes, D., & Smith, M. (1998). Crop evapotranspiration – Guidelines for computing crop water requirements – FAO Irrigation and Drainage Paper 56. Food and Agriculture Organization of the United Nations.
- Busch, J., & Losch, R. (1998). Stomatal behavior and gas exchange of Sedges (*Carex* spp.) under different soil moisture regimes. *Physics and Chemistry of the Earth*, 23(4), 443-448.
- County of San Diego. (2014). *County of San Diego Low Impact Development Handbook*. San Diego, CA: Department of Public Works, Watershed Protection Program, County of San Diego.
- Durner, W., & Iden, S. C. (2011). Extended multistep outflow method for the accurate determination of soil hydraulic properties near water saturation. *Water Resources Research*, 47(8), W08526.
- Harman, C. J. (2015). Time-variable transit time distributions and transport: Theory and application to storage-dependent transport of chloride in a watershed. *Water Resources Research*, 51, 1-30.
- Le Coustumer, S., Fletcher, T. D., Deletic, A., Barraud, S., & Poelsma, P. (2012). The influence of design parameters on clogging of stormwater biofilters: A large-scale column study. *Water Research*, 46(20), 6743-6752.
- Lindsey, G., Roberts, L., & Page, W. (1992). Inspection and maintenance of infiltration facilities. *Journal of Soil and Water Conservation*, 47(6), 481-486.
- Mallants, D., Mohanty, B. P., Vervoort, A., & Feyen, J. (1997). Spatial analysis of saturated hydraulic conductivity in a soil with macropores. *Soil Technology*, 10(2), 115-131.
- Mapa, R. B., Green, R. E., & Santo, L. (1986). Temporal Variability of Soil Hydraulic Properties with Wetting and Drying Subsequent to Tillage. *Soil Science Society of America Journal*, 50(5), 1133-1138.

Appendix C

Supporting Information for Chapter 4

Introduction

This Supporting Information includes further details about the stochastic modeling used to estimate campus runoff volumes (Text S1). Next, we present the results of a set of preliminary simulations used to determine the tank size for our study (Figure S1). We also provide plots of the human and environmental benefits from our study plotted against annual rainfall (Figure S2). References are summarized at the end.

Text S1. Input Details for Campus Runoff Model

The Hydrus 1D model used to estimate runoff volumes from the pervious areas of the UCI campus (assuming a 2 m deep soil profile) requires several inputs, including precipitation, irrigation, evapotranspiration, soil texture, and depth to groundwater. These are discussed below in turn.

- 1) *Precipitation*: Daily precipitation data for January 1, 1990 – December 31, 2016 for scenario P-1 were downloaded from the NOAA NCEI Global Historical Climatology Network, Station ID: GHCND:USC00046175 (Newport Beach, CA). Daily precipitation data (excluding snowfall) were also downloaded for the same timespan from Station ID: GHCND: USC00182325 (Washington, DC). Approximately 6 months of missing data in this dataset were replaced using daily precipitation from another Washington, DC station (Station ID: GHCND: USC00186350). Over these 27-year periods, the annual average rainfall was 23 cm for Newport Beach, CA and 120 cm for Washington, DC. To generate the P-2 rainfall time series, we scaled the daily Washington, DC rainfall by the ratio of the averages (23 cm/120 cm). For both P-1 and P-2, the precipitation amount of each storm event in the time series is perturbed by a precipitation multiplier (randomly sampled from a uniform distribution ranging from 0.8-1.2) for every simulation.
- 2) *Irrigation*: UC Irvine relies almost exclusively on recycled water for irrigation (UC Irvine, 2017). We used historical data (provided by UCI Environmental Planning) of the monthly recycled water consumption at UCI for 1990-2016. Because this dataset does not have daily resolution, the recycled water consumption for each month was divided by the number of days per month to estimate a daily irrigation time series.
- 3) *Evapotranspiration*: We used historical potential evapotranspiration (PET) data from the Climatic Research Unit global dataset (Harris et al., 2014). We specified the Irvine pixel and divided the monthly PET by the number of days per month to estimate a daily PET time series.

- 4) *Soil texture*: Soil type information for the UCI area was determined from the USDA Web Soil Survey. Based on the area of each soil type and the soil texture triangle (USDA NRCS), we determined the minimum and maximum percentages for sand, silt, and clay. Each runoff simulation randomly selects a value from uniform distributions for sand (27.77-51.62%) and clay (38.74-50.66%). The silt percentage is then estimated as 100% minus the sum of the sand and clay percentages for each realization. For each realization, the randomly generated soil texture is then used in Hydrus 1D to estimate the van Genuchten parameters for modeling variably saturated flow.
- 5) *Depth to shallow groundwater*: The distribution of depth to shallow groundwater (a normal distribution with mean 6.45 m and standard deviation 1.65 m) was determined by comparing land surface elevation to shallow groundwater depth for the region (summarized in OCPW, 2013). Each runoff simulation selects a value from this normal distribution.

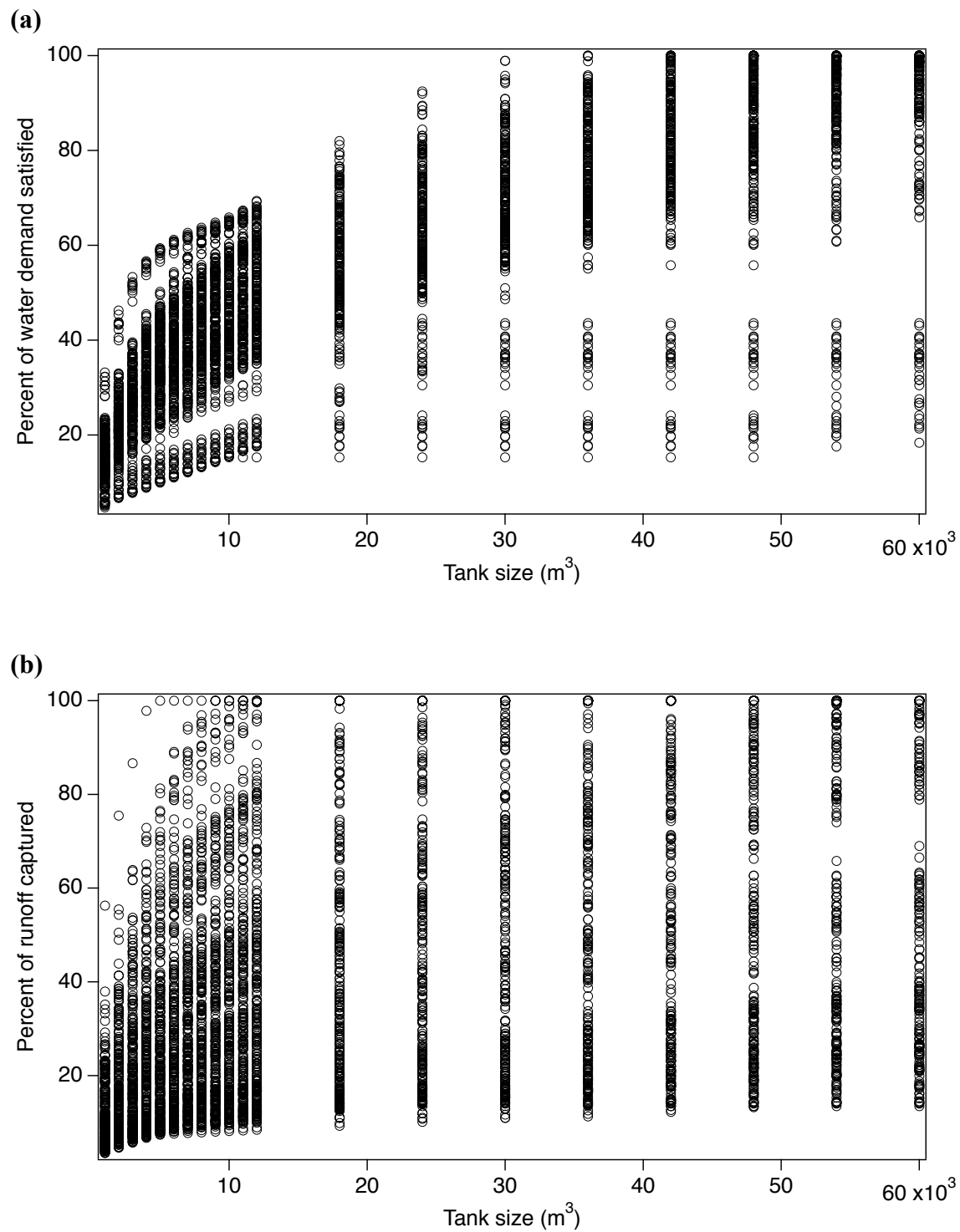


Figure S1. Results of preliminary modeling of human and environmental benefits delivered by a passive control tank with sizes ranging from 1,000 to 60,000 m^3 . We observed diminishing returns in benefits for tank sizes larger than 10,000 m^3 .

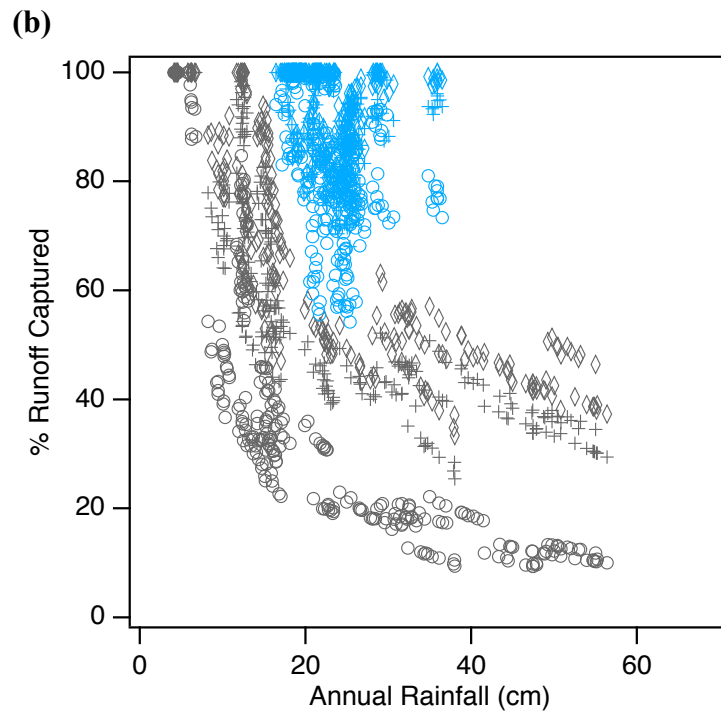
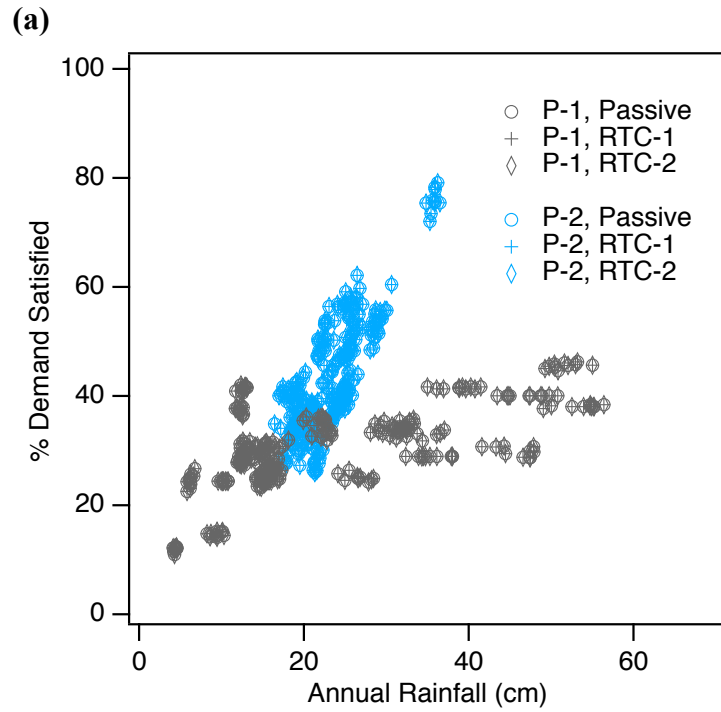


Figure S2. Human and environmental benefits plotted against annual rainfall for the two precipitation scenarios (P-1 and P-2) and three tank scenarios (Passive, RTC-1, and RTC-2) analyzed in the main text.

Appendix C References

Harris, I.; Jones, P. D.; Osborn, T. J.; Lister, D. H. Updated high-resolution grids of monthly climatic observations – the CRU TS3.10 Dataset. *Int. J. Clim.* **2014**, *34* (3), 623-642.

OCPW. Hydrogeologic Characterization and Water Balance Development, Newport Bay Watershed Swamp of the Frogs, Orange County, CA. Prepared for Orange County Public Works by Daniel B. Stephens & Associates, Inc. **2013**.

NOAA National Centers for Environmental Information, Global Historical Climatology Network. <https://www.ncdc.noaa.gov/ghcn-daily-description>

UC Irvine. *University of California, Irvine Water Action Plan*. **2017**. Irvine, CA.

USDA, Natural Resources Conservation Service, Web Soil Survey. <https://websoilsurvey.sc.egov.usda.gov/App/WebSoilSurvey.aspx>