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Performance of Engineered Streambeds for Inducing Hyporheic Transient Storage and Attenuation of Resazurin

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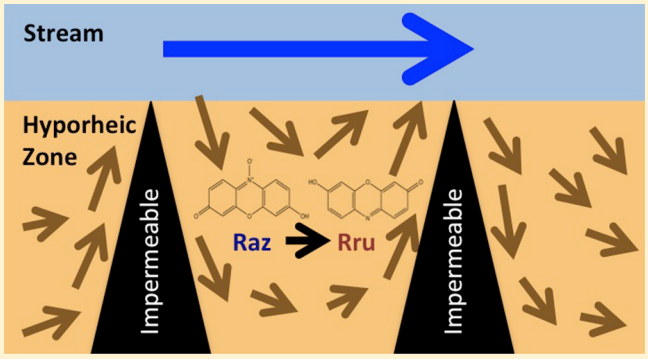
Supporting Information

ABSTRACT: Several U.S. programs provide financial incentives for stream restoration to improve degraded water quality. These efforts prioritize hyporheic zone (HZ) restoration to enhance contaminant attenuation, but no stream restoration or stormwater best management practice (BMP) explicitly tailors hyporheic residence times to target specific contaminants of concern. Here we present the first physical demonstration of a new BMP called Biohydrochemical Enhancements for Streamwater Treatment (BEST). BEST are subsurface modules that use hydraulic conductivity modifications to drive hyporheic exchange and control residence times, combined with reactive geomedia to increase HZ reaction rates. Experiments were conducted in 15-m long outdoor flumes: one all-sand control, the other with BEST modules. Sodium chloride (conservative tracer) and resazurin (surrogate for a reactive pollutant) injections were conducted, with observations analyzed by stream transient storage models. Results demonstrated that BEST increased the effective HZ size and resazurin transformation both by ∼50% compared to the control. Numerical simulations of extended reach lengths showed that BEST could achieve 1-log removal of resazurin in 111 m, versus 172 m in the control, and 414 m and 683 m in two numerically simulated urban streams. These results emphasize the potential of BEST as a novel HZ BMP to improve streamwater quality.



INTRODUCTION

Degraded water quality and poor biological health in U.S. rivers are widely recognized,[1] as is the potential of the streambed hyporheic zone (HZ) to treat many contaminants of concern.[2−6] Hyporheic exchange is a growing focus of stream restoration, but such efforts still typically lack a clear ranking of priorities (e.g., improved streamwater quality, enhanced fish and biota habitat, or aesthetics) and the explicit consideration of physical and/or biogeochemical controls to achieve them.[7−10] Calls to increase hyporheic exchange fluxes during river restoration efforts[3,11] are laudable for promoting the translation of hyporheic science into practice; however, increasing hyporheic exchange fluxes alone may not result in improved reach-scale water quality.[12−17] Rather, many studies have emphasized the importance of matching hyporheic residence times to reaction time scales of interest to optimize contaminant attenuation.[18−23] In brief, hyporheic residence times should be tailored to promote appropriate biogeochemical conditions for the reaction of interest, and ensure the reaction proceeds meaningfully toward completion (e.g., Damköhler number, Da ≈ 1),[13,18,24,25]; however, no study has attempted this in practice.

Different contaminants can have dramatically different reaction time scales,[26,27] especially when site-specific conditions are considered.[6,9] The top three causes of total maximum daily load (TMDL) 303(d) impairment as defined by the Clean Water Act in the U.S. are pathogen indicators, nutrients, and metals (other than mercury).[28] Each of these contaminant classes has different biogeochemical attenuation processes.[29−34] Many contaminants can generally be attenuated under aerobic conditions that are typical of short hyporheic residence times, including pathogens (via sorption and inactivation/predation),[35] metals and soluble phosphorus (via sorption and (co)precipitation),[31,36,37] and ammonia (via oxidation).[38] Conversely, nitrate removal (denitrification) occurs predominantly under anaerobic conditions, which require (1) longer hyporheic residence times to develop in the bulk[19,39] or microzone[40] domains, or (2) mixing with anaerobic groundwater. To further complicate matters,

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hyporheic residence times in field studies span at least 6 orders of magnitude, from seconds to days.[41] With such variability in flow and reaction time scales, the odds are low that the time scales fortuitously align for a given combination of site and contaminant. Unfortunately, there is no hyporheic or stream restoration Best Management Practice (BMP) that explicitly controls hyporheic residence times or stream-groundwater mixing dynamics. Likewise, BMPs intended for stormwater quality improvement have generally ignored the potential of HZ modifications.

A crediting system for hyporheic denitrification via stream restoration was recently established as part of the Chesapeake Bay Nutrient TMDL.[42] This innovative framework grants hyporheic denitrification credits—based on volumetric denitrification rates derived from local studies—to restored subreaches with demonstrated hyporheic exchange.[42,43] However, as stream restoration crediting evolves,[44,45] practitioners need better BMPs to optimize hyporheic treatment of contaminants of concern. For example, cross-vanes (V-shaped rock weirs) are one of the most popular hyporheic restoration BMPs[46,47] and are specifically mentioned by the Chesapeake Bay TMDL program,[42] yet they have minimal impact on in-stream nitrate concentrations at the reach scale.[48,49] Even when cross-vanes drive large hyporheic exchange fluxes, hyporheic residence times tend to be too short to create anaerobic, net-denitrifying conditions.[12] Cross-vanes have other benefits such as channel stabilization, habitat heterogeneity, stream aeration, and improved aesthetics,[46] but the above studies show that their hyporheic denitrification performance is underwhelming. Cross-vanes and similar structures also have minimum spacing requirements depending on discharge and slope (e.g., one structure every 10−200 m of channel length)[46] and create only localized effects,[12,48] restricting the fraction of streamwater that can be treated in a given reach length. Taken together, these constraints suggest that meaningful water quality changes could require tens of kilometers of stream restoration, even in low-order streams.[48,49]

In contrast to surface structures like cross-vanes, direct engineering of streambed sediments with Biohydrochemical Enhancements for Streamwater Treatment (BEST) was proposed as a novel means to enhance hyporheic exchange and modify hyporheic residence time distributions.[50] BEST builds on the concept of using streambed hydraulic conductivity (K) modifications to drive hyporheic exchange.[51−53] Specifically, BEST modules include alternating regions of relatively low- and high-K to drive hyporheic exchange, with reactive geomedia amendments (e.g., biochar, woodchips, recycled industrial materials) within the relatively high-K region to increase contaminant attenuation rates. In a separate study, Pryshlak et al.[54] found that abrupt hydraulic conductivity heterogeneities (analogous to BEST) drive greater hyporheic exchange than gradual transitions, and that in some cases these effects can be more important than bedform-driven exchange at the reach scale. Numerical modeling showed the potential to customize BEST modules to effectively treat various contaminants of concern, including nitrate, especially in small streams.[50] However, BEST modules, and direct modifications of streambed K more generally, have not been tested in a physical system to evaluate whether they increase hyporheic exchange and solute retention at the reach scale. Rather, our current concept of K modifications as drivers of hyporheic exchange is based on electrical analog[51] and numerical hydrologic[50,52] models that either do not simulate water quality changes or include potentially significant simplifications (e.g., neglecting turbulent transport of solute into the hyporheic zone, ignoring small scale variability in sediment topography of flat beds, or representing surface water as a constant head boundary based on hydraulic grade line). Given the possible impact of these assumptions on predicted hyporheic flows and residence time scales,[55−57] and the importance of these factors in maximizing hyporheic fluxes of specific time scales, it is unclear whether the aforementioned models are fit to predict reach scale water quality in actual streams. Data from physical systems are required to evaluate the hydrologic effects of K modifications and provide a basis for improved modeling.

The objective of this study was to test the ability of physical BEST modules in constructed stream flumes to increase reach scale (1) hyporheic exchange, and (2) attenuation of a reactive solute, compared to an all-sand control. However, hyporheic exchange and residence time distributions are difficult to measure in situ due to complex and variable spatiotemporal patterns.[58] Thus, both residence times and hyporheic fluxes at the reach scale are often modeled using a mass transfer approach wherein relatively slow hyporheic exchange flows are represented by immobile transient storage compartments.[59,60] Our analysis was based on mass transfer modeling of conservative (NaCl) and reactive (resazurin, Raz) tracers. While conservative tracers provide information on physical transient storage dynamics, Raz includes information about hyporheic biogeochemical processes as it reduces irreversibly into a transformation product, resorufin (Rru), especially in the presence of actively respiring aerobic microorganisms in hyporheic sediments.[61−64] Raz was ideal for this analysis because its reaction is typically transport-limited, thus it indicates reach-scale effective hyporheic exchange even for short, high-throughput hyporheic flows.[8] Raz may also be used as a metabolic indicator (e.g., of metabolically active transient storage).[8,62] In other words, Raz serves as both (1) a proxy for effective hyporheic exchange to complement conservative tracer data, and (2) a model compound for many other biodegradable solutes.[64] Data from the control and BEST flumes were used to calibrate transient storage models, which allowed us to extrapolate physical results to simulate the impacts of BEST compared to all-sand control, concrete-lined (theoretical), and two actual (from literature) urban channels for water quality over longer reach lengths than could be accomplished in our constructed flume facility. Significant differences in reach scale hyporheic exchange and Raz attenuation between the BEST and control flume, as predicted by previous electrical analog and numerical models,[50−52] would support the use of such models for reach scale predictions of water quality and generally provide a proof of concept for BEST. Conversely, insignificant differences would suggest that BEST modules and/or the models used to design them were not fit for this purpose.

■ MATERIALS AND METHODS

Stream Flume Construction and Operational Conditions. Experiments were conducted in outdoor stream flumes at the Mines Park Water Reclamation Facility at the Colorado School of Mines in Golden, CO. Two identical streams were constructed, each 15-m long, 35-cm wide, at approximately 1% slope, and separately contained within impermeable ethylene propylene diene monomer (EDPM)

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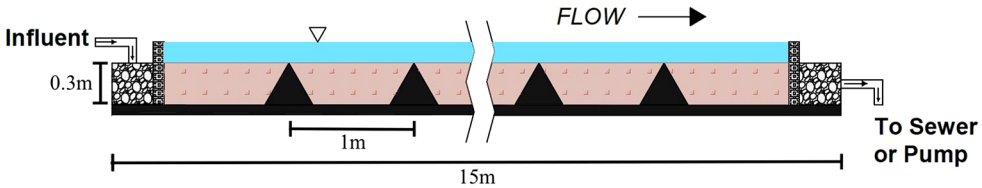

Figure 1. Schematic of BEST stream showing low-*K* blocks (black triangles) in between sand/woodchip geomedia (tan) and gravel boundary conditions. The BEST stream had 13 blocks in total at uniform 1-m spacing. The control stream had identical dimensions, but no low-*K* blocks nor woodchips.

liners. The upstream boundary condition for each flume was a 1-m long, 30-cm deep gravel compartment for flow dissipation, bounded by a 4-cm thick coarse, permeable mesh (Matala U.S.A., Laguna Hills, CA). Downstream boundary conditions at x = 15 m consisted of no-flow walls in the streambed to maintain saturation; surface water spilled over the wall through another coarse mesh. One stream was filled to 30 cm depth with 99.6% silica sand (6/9 Colorado Sand, Premier Silica, Irving, TX) and contained no BEST modules as a control condition ("control"). The other stream utilized custom triangular plastic blocks, caulked to the EDPM, to form impermeable BEST modules ("BEST"). These blocks (13 in total; 29 cm tall, 35 cm wide, and 14.5 cm long at the triangular base), were placed at 1-m intervals from x = 0.5 m to x = 12.5 m in the BEST stream to create 12 BEST modules (sediment regions bookended by impermeable blocks) in series (Figure 1). Notably, the triangular blocks were completely sealed and had no internal flow. The BEST stream was filled to a depth of 28 cm with a mixture of the same silica sand as the control, but also amended with woodchips (Medium Decorative Bark, Permagreen Organics, Arvada, CO) at a ratio of 67/33 v/v, respectively. The BEST stream was topped with 2 cm of silica sand, which completely covered the plastic blocks, and resulted in identical aesthetics for both streams from the surface. Woodchips were included in BEST to provide a long-lasting biofilm substrate and slow-release of dissolved organic carbon for biofilm metabolism.[65−68] The use of woodchips in the BEST stream introduced an additional test variable compared to the control stream (i.e., impermeable walls and media mixture). This is justified for a functional comparison of one potential embodiment of BEST (recognizing that other BEST module designs may incorporate additional media or sand alone) to a reference case, given the time and resource constraints of building physical models at the current scale. The *K* values of the control stream media and BEST stream media were approximately equal (0.48 ± 0.02 cm/s and 0.44 ± 0.01 cm/s, respectively), and the woodchips produced a minor increase in the porosity of the BEST media (0.44) compared to the control (0.39). These differences are minor and are not expected to be controlling factors between treatments.

The flumes were operated continuously with recycled water from an onsite sequencing batch membrane bioreactor (SB/MBR). SB/MBR effluent used in this study is relevant for streams in the western US, which can often exceed 50% recycled water during low-flows.[9,69,70] All SB/MBR effluent, including water diverted into flumes, was eventually sent back to municipal sewers for standard wastewater treatment. SB/MBR effluent was introduced into the flumes using centrifugal pumps (#4011K11, McMaster-Carr, Elmhurst, IL), which were restricted by flow meters to achieve a flow rate of 0.35 L/s in each flume. These outdoor stream flumes were constructed in August 2015 and operated for 3 months. Flow was temporarily halted for 5 months due to winter weather conditions. Both stream flumes were restarted in April 2016 and water was operated continuously with the exception of brief periods of maintenance (e.g., fixing pump leaks).

Specific Conductivity, Resazurin, and Resorufin. To examine transport behaviors, tracer tests with NaCl (99.6%; Diamond Crystal Solar Naturals, Cargill Inc., Minneapolis, MN) and Raz salt (Product #R7017−5G, Sigma-Aldrich, St. Louis MO) were conducted in September 2016. NaCl was used as a conservative tracer to test for differences in transient storage between the BEST and control, whereas Raz and its transformation product Rru were used as indicators to evaluate whether any differences in transient storage between the control and BEST streams could translate into changes in water quality. Further, differences between the transport of NaCl (only sensitive to physical changes from low-*K* blocks) and Raz/Rru (sensitive to physical changes from low-*K* blocks and, possibly, reaction rate changes from woodchips) in each flume could potentially disambiguate the impacts of low-*K* blocks vs geomedia on Raz transformation. Approximately 2.9 kg NaCl and 1.8 g Raz were mixed into 170 L of SB/MBR effluent in a reservoir and dosed into each stream simultaneously for 2 h with a two-channel peristaltic pump (Cole-Parmer, Vernon Hills, IL). Despite identical tubing, the two-channel pump produced slightly different flow rates: 8.4×10^{-3} L/s to the control stream, and 8.2×10^{-3} L/s to the BEST stream, which was accounted for in the Raz and Rru model simulations (discussed below). The injection solution was chosen to produce peak concentrations of 2× background for electrical conductivity (EC) and <300 μg/L (~1.3 μmol) for Raz. Tracer breakthrough curves were monitored at x = 12.5 m in each stream (to minimize effects of boundary condition at x = 15 m), where surface water was funneled using an EDPM sheet to create a "thalweg". EC and temperature were monitored at 1 min intervals using EC/Temperature probes and data loggers (ES-2 and Em-50, Decagon Devices, Pullman, WA). EC was then converted to specific conductivity (SC) to account for changes in water temperature using the following equation:[71]

$$\mathrm{SC} = \mathrm{EC} \times (1 - r \times (25 - T)) \quad (1)$$

where SC is specific conductivity (mS/cm), EC is electrical conductivity (mS/cm), r is a coefficient set to 0.0171,[71] and T is temperature (°C). Triplicate (or more) samples for Raz and Rru were collected using disposable syringes (#309653, BD, Franklin Lakes NJ), immediately filtered through 0.45 μm disposable filters (#28145-485, VWR, Radnor PA), and collected in sterile amber glass vials (Agilent Technologies, Santa Clara CA). Samples were sent on ice to the University of New Mexico overnight for fluorescence spectrophotometry following established protocols.[64] Notably, the established Raz

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and Rru analysis protocol includes an agitation step so that any dihydroresorufin generated by reversible reaction during anaerobic flowpaths[72] was transformed back into Rru prior to quantitation. The timing of sample collection was designed to provide higher frequency data at the start and end of tracer injections based on preliminary experiments (data not shown).

Mathematical Modeling. Tracer breakthrough curves were modeled using STAMMT-L,[60] a one-dimensional dual-porosity transient storage model that can simulate conservative and reactive transport in stream hyporheic zones (see EQs S1−S4 of the Supporting Information, SI).[62,73] At the flow rate in this study, there was no observable surface transient storage (i.e., pools, eddies), so all transient storage identified in the model was interpreted as hyporheic transient storage. First, conservative SC data were used to calibrate the physical exchange models for each stream (i.e., mass transfer rates and relative cross-sectional area of the hyporheic zone). For ease of comparison, observed SC data for each stream were normalized by subtracting average background SC from each time point and then dividing each value by the average peak SC. Normalized breakthrough curves were analyzed in STAMMT-L and separate models for each stream were calibrated using STAMMT-L inverse mode. Stream velocities were observed to be equal for both streams at 6m/min. The models were minimally sensitive to longitudinal dispersivity, so this parameter was set to 10% of reach length (i.e., 1.25m) in both streams following standard practice.[74] The ratio of immobile/mobile domains, β, and mass transfer parameters (e.g., α_1, α_2, α_3) for various mass transfer formulations were varied during the optimization, using sum of squared errors (SSE) of normalized tracer concentrations as the objective functions. Root mean square errors (RMSE) of observed and simulated tracer concentrations were also calculated separately for each model. STAMMT-L provides 12 different mass transfer formulations for exchange between mobile and immobile domains. These formulations were designed to account for different diffusion scales and bed geometries, and are described in detail by Haggerty and Reeves.[60] Fitting of the data with all 11 non user-defined (i.e., not Type 5: a user specified and in our case, arbitrary, multirate series) formulations was attempted, and the seven formulations that converged successfully were compared. Calibrated physical mass transfer parameters (from SC data) were subsequently applied to reactive transport models for Raz and Rru, wherein Raz and Rru reaction rates were calibrated to fit normalized surface concentrations. The reactive transport component of STAMMT-L uses separate reaction rates for each solute in the mobile zone ($\lambda_{m,Raz}$ and $\lambda_{m,Rru}$) and immobile zone ($\lambda_{im,Raz}$ and $\lambda_{im,Rru}$). Reaction rates for both compounds are negligible in the mobile domain, so only the immobile zone reaction rates were calibrated to normalized Raz and Rru data. Given the expected attenuation of Raz, Raz and Rru concentrations at x = 12.5 m were normalized to the calculated concentration of Raz at the injection point. Initial reaction (prior to optimization) and sorption rates for Raz and Rru were taken from Haggerty et al.,[62] which are representative of other calculated values for $\lambda_{im,Raz}$ (other parameters are not consistently reported).[75−78] Raz was assumed to generate Rru at a 1:1 molar ratio and no other transformation products were considered for Raz or Rru degradation.

After calibrating the physical exchange models and immobile zone (hyporheic) reaction rates for Raz and Rru, additional scenarios were simulated to evaluate the impact of BEST over longer stream reaches. First, it should be noted that the control condition used in our experiments can itself be considered a BMP (i.e., a sand filter) for stormwater treatment or stream restoration. Accordingly, it is important to contrast the control and BEST streams to additional baseline conditions. Thus, we considered a concrete-lined channel with no immobile zone (i.e., a typical constructed stormwater channel), and mass transfer parameters from actual urban streams. Concrete-lined conditions ("concrete") are popular for flood prevention and channel stability,[79] and were simulated by making the transient storage ratio, β, arbitrarily low (i.e., 1×10^{-10}, as STAMMT-L cannot run with a value of zero), while setting exchange parameters to arbitrarily slow rates. Second, STAMMT-L mass transfer parameter values for two urban Rocky Mountain streams from Gooseff et al.[80] were also compared to the BEST, control, and concrete channels as illustrative examples (mass transfer parameter values in SI Table S1). Other parameters such as reaction rates, velocity, and longitudinal dispersivity were set equal to the control and BEST streams. These five models were extended to simulate longer stream reaches of several hundred meters, which is a scale more relevant for stormwater management and stream restoration.

■ RESULTS AND DISCUSSION

Specific Conductivity, Resazurin, and Resorufin. The conservative SC breakthrough curves demonstrated that both BEST and control streams had stream velocities equal to 6 m/min (SI Figure S1). Both streams had much longer tails than the theoretical concrete channel, which is indicative of greater transient storage in the former streams. This was expected given the arbitrarily small β value assigned to the concrete channel due to its lack of HZ. However, the BEST stream also exhibited a slightly longer tail than the control. This difference was difficult to discern due to the short reach length of 12.5m, but the time series of SC breakthrough curve values were significantly different from each other (significance level = 0.05, $p = 5.4 \times 10^{-4}$). Additionally, the ratio of BEST/control SC values averaged 0.98 (± 0.1) during the tracer injection, which matched the ratio of injection pump rates. However, BEST/control SC values increased to an average of 1.80 (± 1.4) during the 60 min postinjection, indicative of greater (relative) tailing in the BEST stream due to increased transient storage.

These findings are consistent with Raz and Rru data that were collected simultaneously with NaCl injections. Raz breakthrough curves showed significantly ($p = 7 \times 10^{-5}$) higher normalized peak concentrations in the control stream (0.81 ± 0.01) than in the BEST stream (0.70 ± 0.003) (Figure 2). For reference, our STAMMT-L simulations showed that observed Raz concentrations were already at steady state in both streams, and a STAMMT-L model neglecting Raz degradation (i.e., sorption only) showed that the concentrations in both streams would have been ≥0.95 by t = 120 min without degradation of Raz (Figure S2). Therefore, the gap in normalized peak concentration between the control and BEST, which accounts for slightly different tracer injection rates, showed that both streams attenuated peak concentrations of Raz but the effect was greater in the BEST stream. As expected, neither stream demonstrated substantial tailing of Raz, because transient storage of Raz that would create tailing would presumably cause Raz to decay to Rru. Raz has previously been observed to exhibit minimal tailing, and in natural systems this is generally attributed to biotransformation rather than

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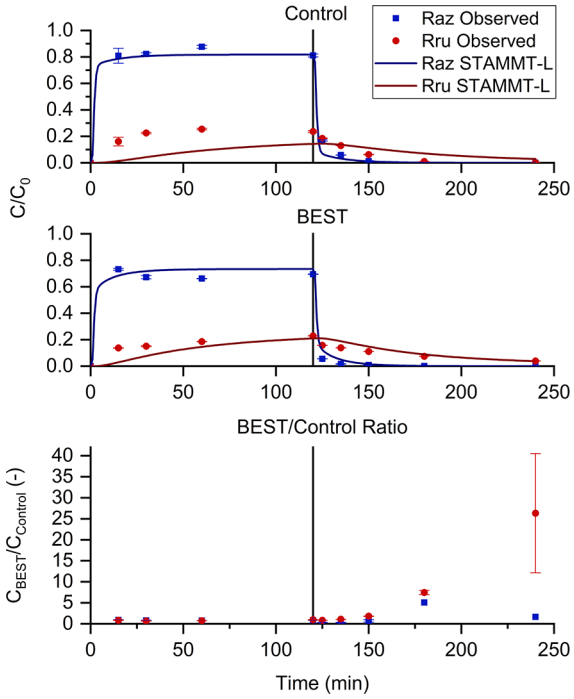

Figure 2. Observed and simulated Raz and Rru breakthrough curves for control (top) and BEST (middle), and BEST/control concentration ratios for Raz and Rru (bottom). Tracer injection ended at t = 120 min (vertical bar). Error bars represent one standard deviation based on triplicate (or more) samples.

irreversible sorption.[81] In contrast, more pronounced tails were observed for the transformation product, Rru, in both streams, and the tailing was particularly pronounced in the BEST stream. This is most evident when comparing the ratio of BEST/control concentrations for Raz and Rru over time. The ratio of BEST/control Raz and Rru concentrations (measured at the end of the reach, x = 12.5 m) both remained approximately 0.8 throughout the injection phase of the experiment (Figure 2). Postinjection, both streams showed rising Rru/Raz concentration ratios indicative of Raz transformation into Rru. Once again, this effect was greater in the BEST stream than that in the control, with BEST/control Rru concentration ratios steadily increasing postinjection to 26.0 ± 14.2 by t = 240 min. Given that Raz degradation is negligible in surface waters,[62] these ratios demonstrate increases in reaction rate and/or transient storage in BEST compared to the control. These data do not allow us to further distinguish between reaction rate and transient storage as controlling factors, because the geomedia (sand/woodchip mixture in BEST compared to all sand in control) and sediment architecture (presence of impermeable blocks in BEST but not control) differed between the BEST and control streams. However, the STAMMT-L results (discussed below) provide additional information to evaluate these relationships.

Tracer Simulations using STAMMT-L. *Mass Transfer Calibration.* The seven mass transfer formulations that converged during calibration all produced reasonable fits to observed data. The models slightly underestimated SC values during the rising limb, but more closely followed the tracer tails (SI Figure S1). Because the data in breakthrough curve tails are especially associated with transient storage,[26] which is the most relevant for our study objectives, we consider the model fits to be appropriate for this analysis. Of the seven converging mass transfer formulations, the power-law and log-normal distributions of first-order mass transfer coefficients generated the lowest SSE for both control and BEST streams (SI Table S1), and the SSE values were within ∼1% of each other for both streams. Thus, the log-normal mass transfer model was selected for further study because it was more parsimonious (two mass transfer parameters compared to three for power law), had lower standard deviations for optimized parameter values, and has been previously shown to match breakthrough curve data well in hyporheic studies.[41,82] Therefore, the parameters optimized for each stream were (1) the ratio of immobile/mobile storage (β), (2) log-normal mean mass transfer rate (μ), and (3) skewness of log-normal mass transfer rate distribution (σ). The RMSE of the log-normal models was 0.048 and 0.055 for the control and BEST streams, respectively. The underestimated rising limbs were the largest source of error in our models, but these fits could not be improved without decreasing the fit to the tracer tails, thereby increasing the overall error.

As shown in SI Table S1, the optimized BEST β value was 54% higher than that of the control. Although the exact magnitudes of each parameter were sensitive to the mass transfer model selected, BEST β values were consistently 34−75% larger than corresponding values for the control stream in the six other mass-transfer model fits. Recall that the β parameter for the flumes was optimized to fit the observed breakthrough curves and was not set *a priori* (as it was for the theoretical concrete channel and urban streams from Gooseff et al.).[80] In other words, the calibrated models estimated that the BEST stream had 54% larger effective HZ size, despite identical flume dimensions. Notably, the impermeable BEST triangles actually reduced the porous media volume in the BEST stream by 10−15%, but more than compensated for this reduction through greater hyporheic exchange. The control and BEST streams had comparable log-normal mean exchange rates (μ) of 0.037 and 0.041 min^{-1}, respectively, but the control stream had considerably less skew (σ): 0.57 versus 0.96, respectively. The triangular blocks were effectively impermeable and thus had no internal flow, so this skewness is not due to slower flow within the "low K" blocks. Instead, the larger skewness in BEST is associated with a greater proportion of relatively long residence times within the sand/woodchip media, likely due to increased effective hyporheic zone depth[41] in the BEST compared to the control.

Raz and Rru Calibration. The log-normal physical exchange models, optimized to fit conservative tracer data for each stream, were used as the starting point for reactive tracer analyses. Raz and Rru degradation rates within the immobile zone were calibrated separately for the control and BEST channels, but the Raz degradation rates ($\lambda_{im,Raz}$) converged to identical values within error (0.0461 and 0.0457 min^{-1}, respectively). Therefore, we used a consistent value of 0.046 min^{-1} for $\lambda_{im,Raz}$ in both streams. This reaction rate is higher but on the same order of magnitude as other reported values,[62,78,83,84] and lower than Argerich et al. after accounting for temperature differences (25 °C for both streams in the current study, 12 °C in Argerich et al.).[75] The Raz models generally fit the observed data points well and had RMSE values of 0.039 and 0.041 for the control and BEST, respectively. Conversely, Rru data were difficult to match within STAMMT-L. Our simulated Rru concentrations were well below the observed values until we assumed no degradation of Rru, as in Blaen et al.[85] The BEST simulations

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then matched the observations reasonably well with an RMSE of 0.051, but the control stream still fit poorly (RMSE 0.088). In particular, the control substantially overestimated the rising limb and tail, and underestimated the peak concentrations. A good fit for Raz but underestimation of Rru (generated 1:1 in our model) suggests a mass balance issue. However, observed Raz+Rru peak concentrations were within an appropriate range: 105% and 92% of injected Raz in the control and BEST, respectively. Therefore, this underestimation of Rru concentrations may have been due to contamination of Raz salt by Rru (generally considered 3%),[61] transformation of Raz to Rru during rapid exchange through surficial biofilms that are too fast to be detected by tracer tests, or underestimation of the Raz to Rru reaction rate. However, the latter could not be increased without sacrificing the model fits to Raz data.

Haggerty et al.[62] found the Rru degradation rate constant within the HZ ($\lambda_{im,Rru}$) to be the largest reaction rate constant in the Raz-Rru system. However, our current experiment and others (e.g., Blaen et al.)[85] indicate Rru degradation to be negligible. More research is needed to understand Rru degradation reaction(s) and the conditions in which they are relevant. A recent study successfully measured Raz and Rru degradation rates in situ and found them highly variable with space and depth.[78] Notably, the method from Knapp et al.[78] is based on 1D (vertical) flow as a simplifying assumption. BEST modules are predicted to have 2D flow, with vertical and longitudinal velocities of approximately equal magnitude,[50] which prevented us from calculating spatially discrete reaction rate measurements based on the same method. Ultimately, Rru was not critical to our study because Raz provided a well-characterized model compound. Therefore, as in González-Pinzón et al.,[81] we proceeded with the Raz models, but did not continue Rru simulations. Rru reaction mechanisms and rate constants are more complex and less well-characterized than Raz[81] and should be investigated further in future studies.

Extended Reach Lengths. Differences between calibrated BEST and control models became more obvious when reach length was increased to simulate a length more realistic for implementation into an actual urban stormwater channel (i.e., 100−300 m). Figure 3 shows simulated steady-state Raz concentrations as a function of reach length for calibrated BEST and control stream models, the simulated concrete channel, and two simulated urban streams (Jackson Hole and Teton Pines), where STAMMT-L parameters were previously determined by Gooseff et al.[80] As observed by Johnson et al.,[86] steady-state Raz concentrations were inversely related to β; with larger transient storage ratios resulting in lower downstream Raz concentrations in the mobile (surface) domain. The simulated concrete channel showed negligible Raz transformation, even at extended distances (C/C_0 = 99.6% at x = 300 m) demonstrating that the concrete channel primarily conveyed Raz without attenuating it due to the lack of hyporheic transient storage. This is consistent with literature describing minimal transformation of Raz in surface waters over experimental time scales,[61] and underscores the efficacy of hyporheic transient storage treatment in the other simulated channels. Both the control and BEST stream simulations demonstrated substantial Raz attenuation, but BEST presented a clear improvement relative to the control. Notably, BEST achieved 1-log removal of Raz at approximately 111 m, compared to 172 m for the control. In other words, a control stream needed to be 55% longer than a BEST stream to achieve 1-log removal. However, the control stream itself could be considered a sand filter BMP. Thus, it is not surprising that the control also exhibited substantial Raz attenuation, or that both urban streams from Gooseff et al.[80] provided intermediate water quality benefits relative to the control and simulated concrete channels. These modeled example urban streams—Jackson Hole and Teton Pines—would require 414 m and 683 m, respectively, to achieve 1-log Raz removal. These longer distances are due primarily to the smaller β terms, which are only 12% and 8% of the control value, respectively. Despite the problems inherent in applying the urban streams' mass transfer parameters to a smaller scale, these illustrative examples highlight the vast β parameter space between the concrete and control channels, which otherwise serve as traditional end members.

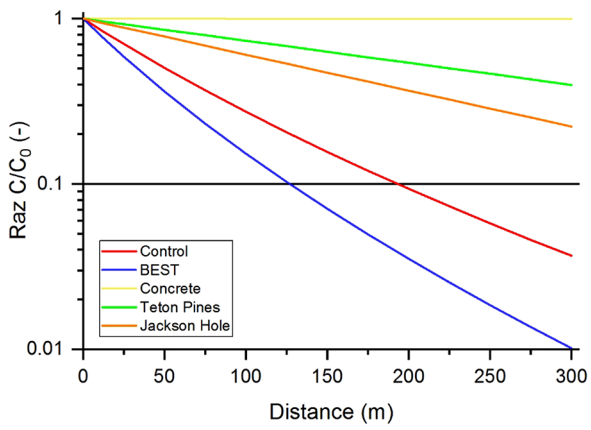

Figure 3. Steady-state Raz concentrations as a function of downstream distance in simulated control, BEST, concrete, and urban channels (Teton Pines and Jackson Hole Golf Streams; Gooseff et al.[80]).

Distinguishing the Effects of Impermeable Walls vs Geomedia on Raz Transformation. BEST increased the effective hyporheic transient storage by 54% compared to the control condition, and greatly exceeded other reference cases: two previously characterized Rocky Mountain urban streams and a simulated concrete channel. Additionally, this increased transient storage translated into correspondingly (58%) greater Raz transformation (based on steady state flume concentrations) compared to the control. The BEST stream had two components that were not present in the control: impermeable barriers at 1m intervals and sand/woodchip geomedia (of approximately equal hydraulic conductivity and porosity as the sand in the control). The former could affect physical flow geometry, while the latter could alter reaction rates. We distinguished between these two components by separately calibrating the mobile-immobile exchange parameters and the reaction rates for Raz and Rru in each stream. The BEST stream had greater transient storage than the control, but, surprisingly, the Raz degradation rate constants were equal at 4.6×10^{-2} min^{-1}. These data show that the increase in Raz attenuation was explained by differences in transient storage between the two streams rather than reaction rates. Therefore, the impermeable walls were the more important design feature in this experiment. However, the woodchip-sand media used in this study was one of many potential geomedia; other geomedia may be more impactful for Raz transformation rates, and woodchips may be an effective amendment for other reactions.

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Considerations for BEST Design and Application. This paper presents the first demonstration of BEST in a physical system. Our results serve as a proof of concept regarding BEST modules by showing that the physical system increased reach scale hyporheic exchange and reactive solute attenuation as predicted by previous numerical models.[50] Given that Raz serves as a model for microbial respiration,[64] our results indicate that aerobic biological attenuation of contaminants (e.g., ammonia,[38] biochemical oxygen demand,[87] phosphorus,[88] phthalates and polycyclic aromatic hydrocarbons,[89] and glyphosate[90]) within the HZ may be improved by the BEST modules used in this study. The current BEST modules may also target anaerobic reactions like denitrification, but other designs may be more optimal. Specifically, BEST modules have potential to increase hyporheic residence time distributions via (1) greater spacing of low-K regions to control flowpath lengths, and (2) selection of geomedia with slightly lower permeability for the (relatively) high-K regions to control pore water velocities. Future studies could evaluate the potential of physical BEST modules to control residence times and redox conditions of hyporheic exchange as modeled in Herzog et al.,[50] thereby evaluating diverse BEST configurations to tailor treatment to specific contaminants of concern.

Reach scale water quality improvements depend on numerous factors including stream discharge and the number of BEST modules in series. BEST is intended for applications in low-discharge streams including small urban catchments and stormwater channels with flow modulation (i.e., downstream of detention ponds). The potential for high density installation of BEST modules (e.g., one module every 1−5 m of channel length) can maximize hyporheic restoration outcomes as compared to existing BMPs such as cross-vanes. Hester et al.[49] estimated that cross-vanes at 50 m spacing could achieve 30% nitrate removal in a ∼1 km, second order stream reach if (1) sediments were highly permeable, and (2) background surface-groundwater pressure gradients were near neutral (or the stream was lined). Optimized BEST modules with geomedia designed to attenuate nitrogen could be placed in series between cross-vanes (e.g., every 1−5 m of channel length), increasing the density of hyporheic restoration by an order of magnitude. In this case, in-stream hyporheic restoration could conceivably provide >30% nitrate removal over reach lengths of hundreds of meters rather than kilometers. BEST may be even more impactful for aerobically attenuated contaminants that are modeled by Raz, as our study simulated Raz removal of >90% in only 111 m of stream length. In both cases, BEST may be a complementary BMP to improve water quality in restored streams and urban stormwater channels.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b01145.

Mass transfer parameters, conservative tracer breakthrough curves, and select relevant STAMMT-L equations (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

BEST	Biohydrochemical Enhancements for Streamwater Treatment
BMP	Best Management Practice
EC	Electrical Conductivity
EDPM	Ethylene Propylene Diene Monomer
HZ	Hyporheic Zone
K	Hydraulic Conductivity
Raz	Resazurin
Rru	Resorufin
SB/MBR	Sequencing Batch Membrane Bioreactor
SC	Specific Conductivity
TMDL	Total Maximum Daily Load

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