Final Technical Report

Title: Seasonal controls on dynamic hyporheic zone redox biogeochemistry

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Executive Summary

The hyporheic zones of upland rivers play a critical role in the processing of solutes, with implications for downstream water quality. Seasonal hydrology controls the expansion and contraction of these zones of mixing, with greater downwelling oxic river water influence during periods of peak river discharge (linked to snowmelt), and greater influence of upwelling anoxic groundwater during periods of low- and base-flow. Through this work, we aimed to quantify upwelling and downwelling fluxes across seasons and assess the impact of these dynamics on microbial community assembly and geochemical gradients at East River, Colorado. Further, we performed high spatial resolution sampling to capture heterogeneous mixing patterns around a characteristic meander on the river and developed reactive transport models to explain seasonal patterns of manganese (Mn) cycling in riverbed sediments.

We were able to measure a dominant period of downwelling river water associated with high river discharge in Spring 2017 that led to the mixing of microbial communities across a 60-cm depth profile through the riverbed at three locations around the meander, and higher rates of aerobic respiration via delivery of dissolved oxygen (O_2) and dissolved organic carbon (DOC). Conversely, we demonstrated that depth-resolved microbial communities became more distinct and stratified across a depth gradient during periods of low- and base-flow when upwelling groundwater exerted more influence in the riverbed. We also observed an increase in Mn concentrations within deeper streambed sediments during the baseflow season.

To understand how changes in river water and groundwater mixing influenced Mn cycling, we developed one-dimensional reactive transport models over the annual hydrograph. In field observations and models, dissolved Mn is flushed from the streambed during spring snowmelt. A shift to upwelling conditions over the subsequent baseflow period allows for groundwater rich in dissolved Mn to mix with oxygenated river water in the shallow subsurface, resulting in net accumulation of Mn-oxides until the bed freezes in winter. We also developed models for hydrograph scenarios with snowmelt events of various size and timing. Our scenarios suggest that in years with less snowpack and a longer baseflow season, Mn oxidation will be favored in the upper riverbed sediments over more of the year, which may increase the sorption capacity of the streambed for other metals.

In addition, we assessed fine-scale geochemical and hydrologic heterogeneity in the meandering riverbed by sampling pore water at 20 cm depth across more than 100 locations in August 2018. Sample locations span distinct zones of up-welling groundwater that contrast against dominant down-welling conditions. Clear differences in carbon quality and concentrations of redox

sensitive solutes were detected between these zones, highlighting the importance of understanding heterogeneity across plot-scale sampling domains. These geochemical differences were associated with differences in microbial assemblage, but microbial diversity was generally uniform and high across all locations at the same depth, regardless of the extent of groundwater influence.

Results

1. Riverbed mixing patterns are influenced by seasonal hydrology in an upland watershed

The mixing of oxic river water and (generally) anoxic groundwater creates highly reactive interfaces in riverbed environments. To understand temporal variability in water mixing patterns, in situ, depth-resolved temperature probes were installed at three locations around a characteristic meander (Meander A) on the East River in Colorado. The decay of diel temperature variability with depth in the riverbed enabled estimates of up-welling and down-welling conditions at 15-minute intervals. The processing of these data indicated that spring snowmelt and runoff in the East River catchment drove a period of sustained down-welling river water, while up-welling of groundwater or older river water was the dominant influence of riverbed hydrology during most of the year (**Figure 1**).

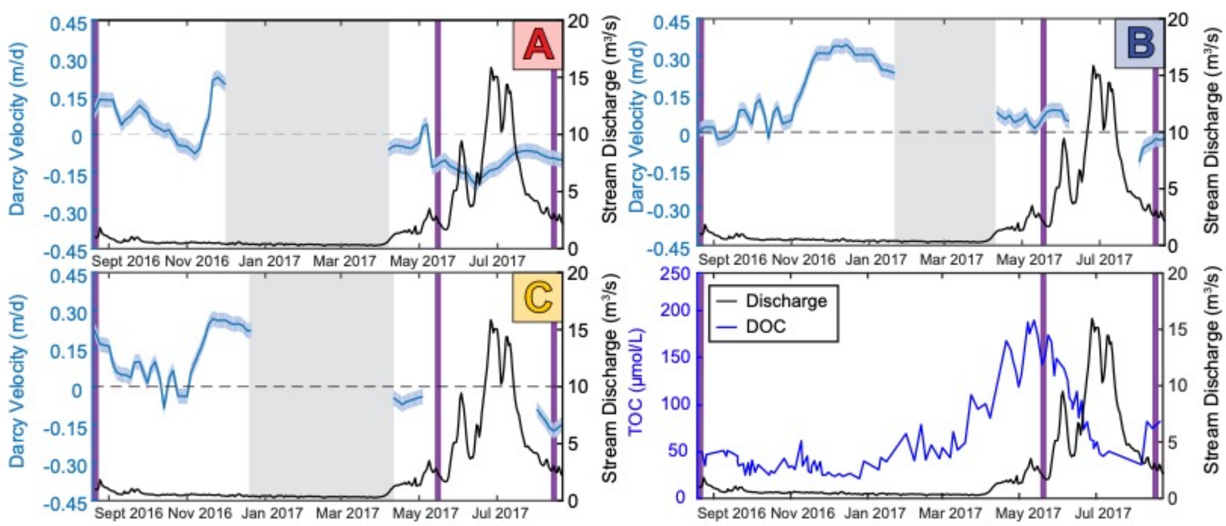

Figure 1. Vertical fluid fluxes (Darcy velocities) for three locations around Meander A on East River (A, B, and C), as well as DOC vs. stream discharge (4th panel). Positive Darcy velocities represent upwelling and negative Darcy velocities represent downwelling. Purple lines indicate sampling campaigns and gray boxes indicate periods of streambed freezing when data could not be collected.

These results were complemented by strontium isotope measurements (performed by John Christensen at Lawrence Berkeley National Laboratory), which indicated that streambed mixing patterns were highly heterogeneous in the cobble-rich streambed, with sampling location B more influenced by a groundwater end-member with a high $^{87}Sr/^{86}Sr$ ratio, and locations A and C more frequently influenced at depth by fluids with lower $^{87}Sr/^{86}Sr$ ratios indicative of older river water on longer hyporheic flow paths (**Figure 2**). These results were also consistent with location B having greater rates of groundwater upwelling over the base flow period and a shorter frozen period in winter (**Figure 1**).

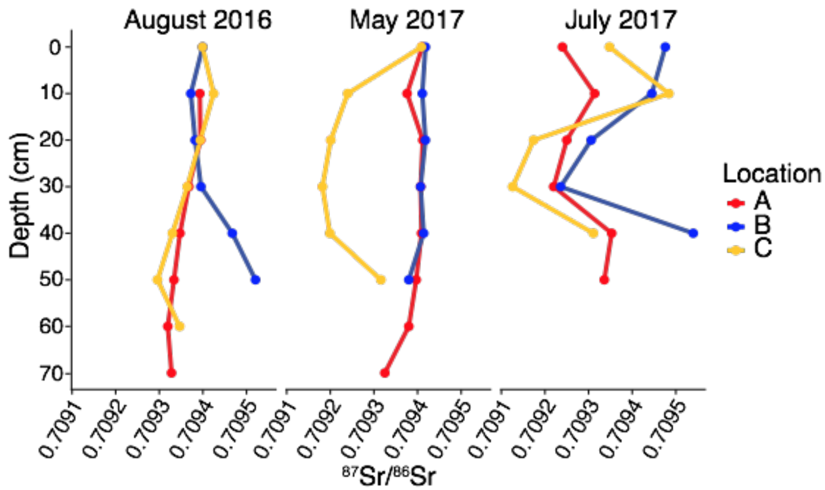

Figure 2. Strontium isotopic composition for samples collected during each season and location across the 70 cm depth profile.

Down-welling river water acted to introduce O_2 and DOC into the riverbed, stimulating microbial aerobic respiration. The highest rates of microbial respiration were detected during high river discharge and associated down-welling conditions (**Figure 3**).

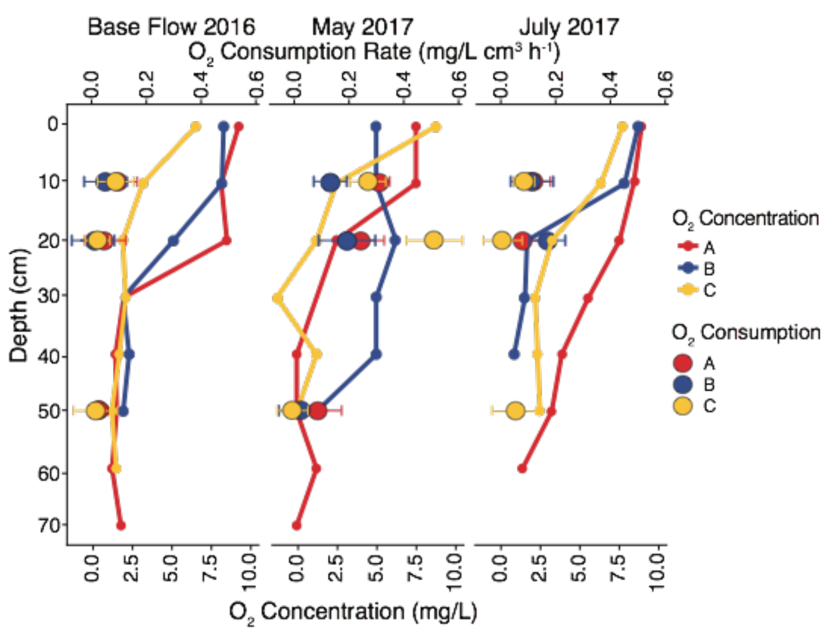

Figure 3. Dissolved oxygen consumption (mg/L • cm^3 • h^{-1}) and concentration (mg/L) across a 70 cm depth profile at each location. "Base Flow 2016" measurements were collected in October 2016 rather than August 2016 due to infrastructure constraints.

Based on Location B, where geochemical transport appeared to be well-described by vertical processes, we modeled the reactive transport of Mn, DO, DOC, and a conservative "solute" (specific conductivity, SpC) using COMSOL. Modeled specific conductivity profiles were in good agreement with measurements (**Figure 4**, left). Specific conductivity decreased in May as stream water intruded during the rising limb of the spring snowmelt event, then increased in association with groundwater upwelling (Figure 4, left). The model also captured the increase in O_2 and decrease in dissolved Mn in May during downwelling conditions (**Figure 4**, center and right). Although modeled O_2 concentrations decayed faster with depth than observations (especially in May), our sampling technique exposed samples to O_2 from the atmosphere, so measured O_2 concentrations represent maximum estimates of in-situ concentrations. The model accurately characterized shifts in the dissolved Mn concentration profile over July and August (**Figure 4**, right).

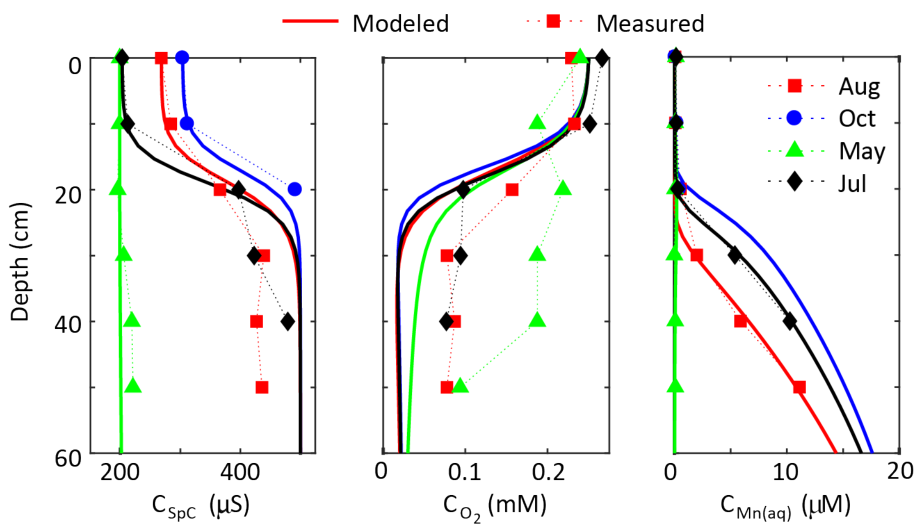

Figure 4. Comparison between measured and modeled results for specific conductivity (SpC), O_2, and $Mn_{(aq)}$ using the field model at location B.

Under the observed hydrograph scenario, model results show that low-conductivity river water mixes deeper into the streambed over the rising limb of the spring snowmelt (April through mid-May), delivering DOC that stimulates both aerobic and anaerobic respiration. The greatest dissolved Mn fluxes to the river occur during this period when river discharge and hyporheic exchange rates are high, despite overall downwelling conditions in the streambed (**Figure 5**). Over the recession and baseflow season (mid-June through Feb), river water penetrates less deeply, and upwelling groundwater supplies dissolved Mn to shallower pore water, leading to high accumulation rates of Mn oxides in the shallow streambed. Fluxes of Mn to surface water are moderate. Entering the winter season, the streambed freezes, and both Mn cycling and the flux of Mn to surface water become negligible. We also explored these Mn dynamics under a warmer scenario with a shorter frozen period, earlier spring snowmelt event of smaller magnitude, and longer baseflow season (**Figure 5**). Rates of Mn oxidation and Mn flux the stream are greater over a longer baseflow season with more groundwater discharge, while the rate of Mn reduction and supply of Mn to the stream are both smaller during the snowmelt season. These results have important implications for the timing of Mn export from alpine streams under a changing climate and the behavior of other trace metals, which sorb to Mn oxides in streambeds.

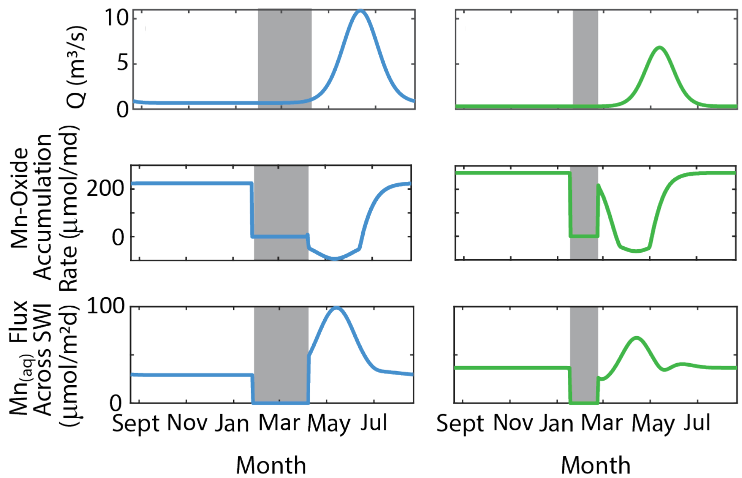

Figure 5. Model results for two hydrologic scenarios: Present (left), Warming (right). Stream discharge (Q) is shown above. Gray shading indicates frozen streambed conditions. Mn-Oxide Accumulate Rate reflects changes in the pool of Mn oxides within the upper 50 cm of streambed sediments. Positive values of Mn Flux indicate upward transport of dissolved Mn from aquifer to stream.

2. Groundwater-River water mixing patterns influence microbial community assembly

Microbial communities in the streambed were interrogated using 16S rRNA gene analysis of depth resolved pore water-sediment slurries. Although no strong depth- or location-dependent trends were observed in any of the alpha diversity metrics, the comparison of samples across seasons revealed differences. Samples collected during base flow (August 2016) were overall less taxonomically and phylogenetically diverse than spring flood (May and July 2017) samples, suggesting that the river water downwelling may act to introduce microorganisms into the streambed and thus drive increases in community diversity. Additionally, the introduction of O_2 and DOC into the streambed from surface water may have acted to stimulate growth of more diverse microbial assemblages and therefore increase alpha diversity. While microbial communities detected in August 2016 (base flow) varied significantly with those from May 2017 and July 2017 (higher flow), communities detected in May 2017 and July 2017 did not vary significantly from each other. Beta-dispersion calculations that measure the differences between communities in a given grouping revealed a higher value for samples collected in August 2016 (base flow conditions) relative to spring flood samples collected when there was a greater influence of river water in the bed. This suggests that infiltrating river water may have a 'homogenizing' effect throughout the river bed, resulting in microbial communities that are somewhat similar to each other across the depth transect. Conversely, during base flow conditions, upwelling groundwater may drive greater geochemical stratification across the depth profile, resulting in more dissimilar microbial communities.

To further this idea, we investigated how microbial community assembly processes varied across time-points and sampling locations. The assembly of microbial communities is governed by a range of stochastic and deterministic processes including the dispersal of microorganisms, random mutations within the community, and forcings from environmental conditions. Dominant ecological processes acting upon microbial communities can be investigated via null modeling. Briefly, this technique performs pairwise comparisons between measured microbial communities, and determines whether any two communities are more similar or more dissimilar than would be expected by random chance. These analyses revealed that all the communities, regardless of location or sampling time-point, were more similar to each other than would be expected by random chance, and were therefore mostly influenced by homogenizing selection

(**Figure 6**). Given the gravel-dominated and hence highly porous and permeable streambed in the East River, we hypothesize that hydrologic mixing leads to homogenization of the communities across a ~50 cm depth transect. Furthermore, samples collected in August 2016 under base flow conditions had the least-negative ßNTI values, indicating that these communities were least influenced by homogenizing selection (**Figure 6**). This observation tallied with the aforementioned beta dispersion calculations, which suggested that under base flow conditions streambed microbial communities exhibited a greater degree of dissimilarity.

These results were compared to similar calculations performed on depth-resolved streambed microbial communities in the Colorado River, near Rifle, CO, which is an approximately 1,400 meter decrease in elevation from the East River sampling locations. In comparison to the East River, the Rifle sediments have a similar porosity but much smaller grain size, and permeability is expected to be orders of magnitude lower (**Table 1**), highlighting the expected relationship between grain size and altitude along river networks. Reflecting the physical differences between the two systems, depth-resolved communities in the bed of the Colorado River were strongly influenced by variable selection (ßNTI values > 2), indicating that these microbial populations were more dissimilar than would be expected by chance (**Figure 6**). We hypothesize that physical streambed characteristics, namely lower permeability, limit the extent to which fluid-entrained microbes can travel, resulting in more spatially constrained communities. Supporting this inference, homogenizing selection was found to play a significant role in microbial community assembly in Columbia River sediments near Hanford, WA. In contrast to the Colorado River, the sampling location in the Columbia River is characterized by high permeability owing to the Hanford formation underlying the Columbia River (**Table 1**).

	East River	*Colorado River (near Rifle, CO)*	*Hanford Formation*
Porosity (%)	27	30	
D_{50} (mm)	13.26	0.120	
% Mud (< .063 mm)	1.7	23.9	
% Sand (.063- 2 mm)	11.0	70.6	
% Gravel (> 2 mm)	87.3	5.6	
Permeability (m^2)	$10^{-8} – 10^{-5}$	$10^{-12} – 10^{-8}$	$10^{-9} – 10^{-8}$

Table 1. Grain size and porosity data for East River and Rifle streambed sediments.

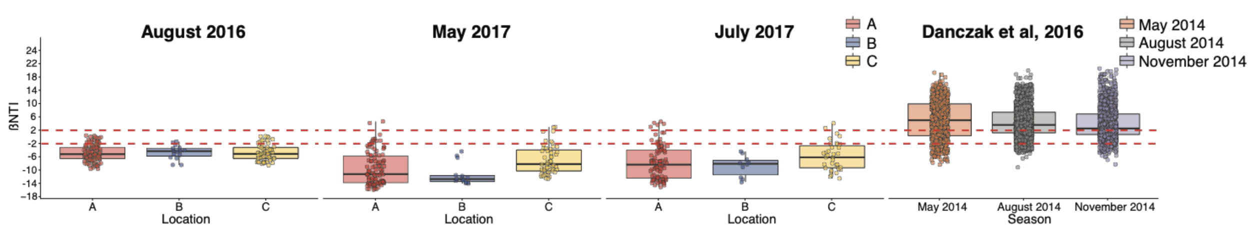

Figure 6. ßNTI for each location and each season. Seasonal values from Danczak et al. (2016) provided for comparison. Dashed red lines indicate selective pressure delineations; ßNTI > 2 = variable selection, ßNTI < -2 = homogenizing selection, |ßNTI| < 2 = stochastic process domination.

3. Heterogeneity in hydrology, geochemistry, and microbial communities during base flow

More than 100 distributed pore water samples collected during the base flow season shed light on patterns of river water-groundwater mixing over a characteristic meander. In the upstream portion of the reach, the cutbank was characterized by a downwelling conditions (negative vertical head gradient, or VHG) and had a high degree of river water mixing (**Figure 7**). In contrast, the point bar in the downstream portion of the reach was characterized by more neutral to upwelling conditions and a greater amount of groundwater mixing. These patterns of river water-groundwater interaction in the channel are consistent with intrameander flow through the floodplain (**Figure 7**).

Variations in river water influence gave rise to clear trends in redox-sensitive solute concentrations, including O_2 and dissolved Mn. Dissolved oxygen concentrations tended to be greater in more river-influenced locations, while Mn concentrations tended to be greater in groundwater-influenced locations. DOC concentrations ranged widely. Some streambed locations had DOC concentrations below river water or more groundwater-influenced sites, potentially indicative of respiration, while other locations had greater concentrations potentially indicative of desorption from streambed organic matter. The quality of dissolved organic matter (DOM) was measured using fluorescence and varied along the continuum of river water-groundwater influence. More groundwater-influenced locations have a higher humification index (HIX) and fluorescence index (FI) (**Figure 8**). The interpretation is that DOM in more groundwater-influenced locations is more complex and microbial in origin, while DOM in more river water-influenced locations is more labile and terrestrial in origin.

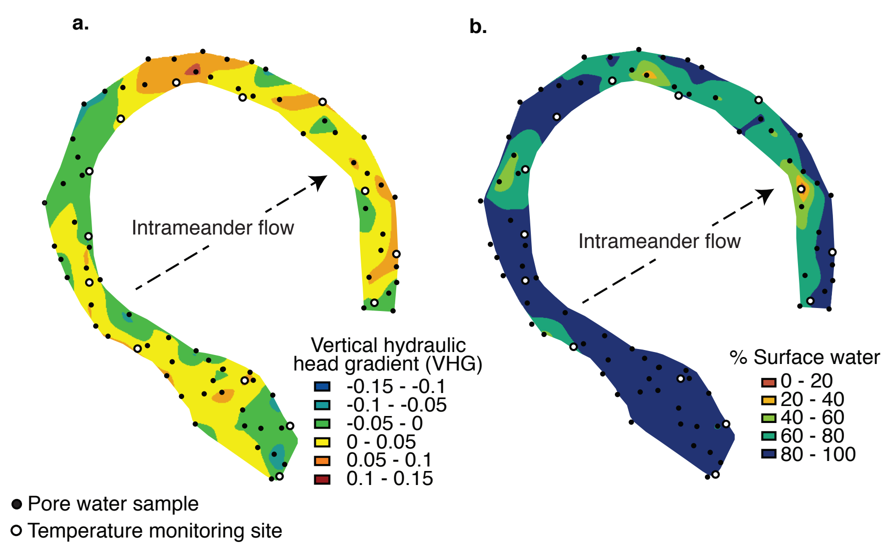

Figure 7. Intrameander flow leads to meander-scale patterns in vertical head gradient (VHG, a) and surface water-groundwater mixing (b) in the streambed at 20 cm depth. Flow direction in the channel is clockwise.

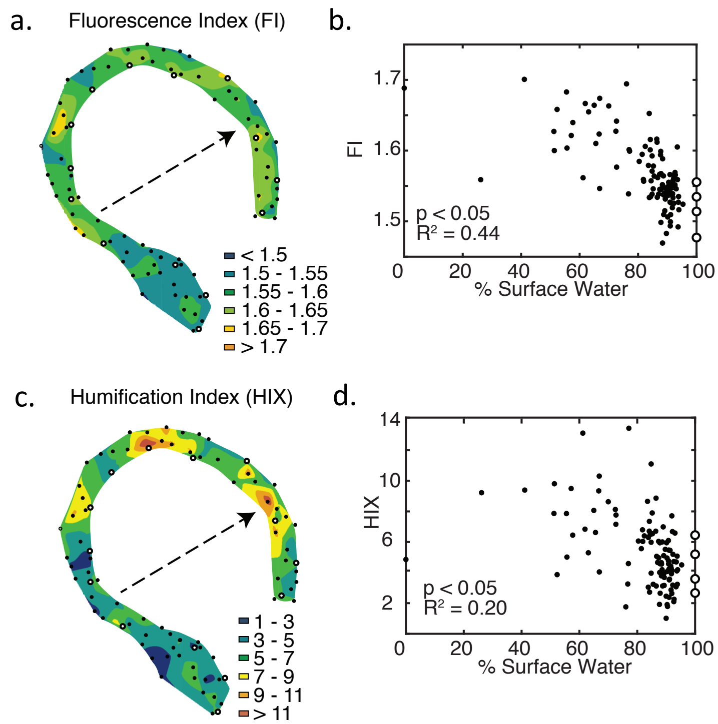

Figure 8. Spatial patterns of fluorescence indices used to quantify DOM quality in streambed pore water: fluorescence index (FI, a and b), and humification index (HIX, c and d). Flow in the channel is clockwise. Stream water samples in right plots are denoted with open circles.

Heterogeneity in river water-groundwater mixing and pore water chemistry was associated with differences in microbial community assemblage. For example, the presence of Atribacteria, Desulfatiglans, and Deltaproteobacteria was associated with groundwater-related variables such as greater specific conductivity, a greater concentration of Mn, and higher HIX (more complex DOM). Despite these differences, all communities were similarly diverse, as measured using Faith's PD, Shannon's H, and Species Richness (**Figure 9**). One possible explanation is that sediments at 20 cm may be exposed to similar amounts of river water influence over other times of year outside our sampling period (particularly during spring snowmelt), leading to uniformly high diversity compared to deeper sediments.

Publications from DE-SC0016488 (submitted or in preparation)

Bryant SR, Briggs MA, Saup CM, Wilkins MJ, Nelson AR, Christensen JN, Williams KH, and Sawyer AH. (in preparation) Seasonal manganese transport in the hyporheic zone of a snowmelt-dominated river (East River, Colorado). *Hydrogeology Journal*, in preparation (pdf available upon request).

Nelson AR, Gabor RS, Saup CM, Bryant SR, Harris KD, Briggs MA, Williams KH, Wilkins MJ, and Sawyer AH. (submitted) Heterogeneity in hyporheic flow, pore water chemistry, and microbial community composition in an alpine streambed. *Journal of Geophysical Research—Biogeosciences*, submitted.

Saup CM, Bryant SR, Nelson AR, Harris KD, Sawyer AH, Christensen JN, Tfaily MM, Williams KH, and Wilkins MJ. (submitted) Hyporheic zone microbiome assembly is linked to

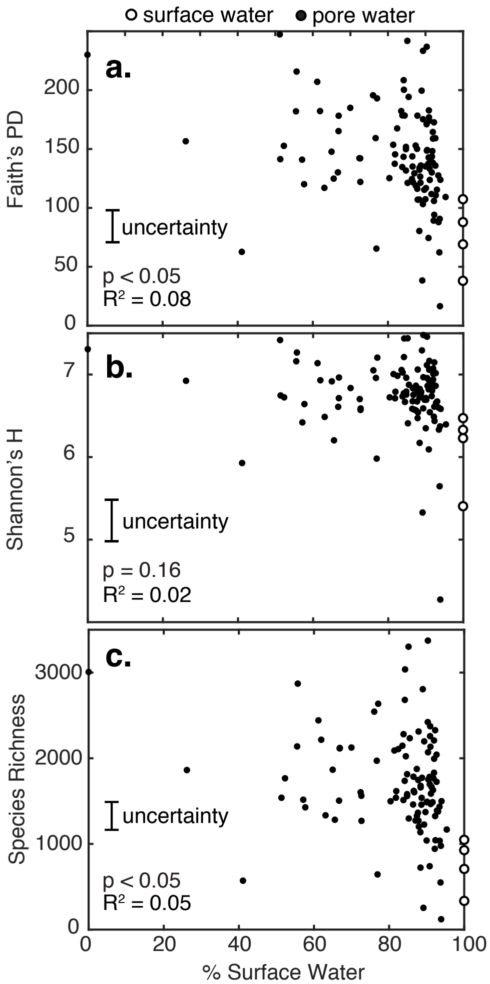

Figure 9. There is little relationship between the mixing of surface water and microbial diversity at 20 cm depth in the hyporheic zone during baseflow, though pore water tends to have higher diversity than surface water. The standard deviation of four surface water samples (open circles) was used as a proxy for uncertainty.

dynamic water mixing patterns in snowmelt-dominated headwater catchments. *Journal of Geophysical Research–Biogeosciences*, submitted.

Open data from DE-SC0016488

Bryant S, Briggs M, Nelson A, Saup C, Wilkins M, Williams K, and Sawyer A. (2019): Estimated Darcy Velocities Using Temperature Time Series for Meander A of East River, Colorado. Seasonal controls on dynamic hyporheic zone redox biogeochemistry. Ess-dive-6678f7bc54ca137-20190304T232135769. doi:10.15485/1498798.

Nelson A, Saup C, Gabor R, Bryant S, Harris K, Williams K, Wilkins M, Sawyer A. (2019): Distributed hydrological, chemical, and microbiological measurements around Meander A of East River, Colorado. Seasonal controls on dynamic hyporheic zone redox biogeochemistry. Ess-dive-c5682778c06cdad-20190411T203213225.

Saup CM, Bryant SR, Nelson AR, Harris KD, Sawyer AH, Christensen JN, Tfaily MM, Williams KH, and Wilkins MJ. (2019): Depth-resolved seasonal porewater chemistry measurements from 3 locations around Meander A of the East River, Colorado. Ess-dive. United States: N. p., 2019. Web. doi:10.15485/1504779.