Authors response to Interactive comment on "Co-located contemporaneous mapping of morphological, hydrological, chemical, and biological conditions in a 5th order mountain stream network, Oregon, USA" by Adam S. Ward et al.

Referees' comments in bold type. Authors responses below each comment.

Anonymous Referee #1
Received and published: 19 June 2019
Review of: Co-located contemporaneous mapping of morphological, hydrological, chemical, and biological conditions in a 5th order mountain stream network, Oregon, USA Ward et al. Summary: This field study was focused on an extensive 62 site, multi-day low flow sampling campaign across a 1st through 5th order river network. This study is unique in that it presents a physical, chemical, and biological dataset at a relatively high resolution spatial extent. This dataset will certainly be used extensively by this group and others to investigate spatial characteristics and drivers of riverine dynamics. My major comment is the lack of context for this study. The introduction is short and does not present the state of the science for this type of research. As described in further detail in major comments below, I believe this manuscript will provide a larger impact in our community with the addition of a brief explanation of where our scientific community is in regards to our understanding of spatial physical, chemical, and biological characteristics of river networks. In addition to this, I included a handful of minor comments that I believe can improve the manuscript.

> No response to the comments above, as this is a summary of more detailed points that are address individually below as "major comments".

Major Comments:
Introduction: The introduction is short and leaves out important context. There have been a range of studies recently that have investigated spatiotemporal river network dynamics. These studies have mostly focused on hydrology or chemistry across river networks that range stream orders. This manuscript builds on those previous studies by incorporating not just hydrology and chemistry, but biology as well, in this spatial assessment. This manuscript and presentation of this dataset has the potential to be more impactful with a brief introduction of the current state of this work. See below for suggestions for several recent papers, although there are an extensive set of related papers on this topic:
Hale, R. B., Godsey, S. (2019). Dynamic stream network intermittence explains emergent dissolved organic carbon chemostasis in headwaters. Hydrological Processes.
McGuire, K. J., Torgersen, C. E., Likens, G. E., Buso, D. C., Lowe, W. H., & Bailey, S. W. (2014). Network analysis reveals multiscale controls on streamwater chemistry. Proceedings of the National Academy of Sciences, 111(19), 7030–7035. https://doi.org/10.1073/pnas.1404820111
Zimmer, M. A., & McGlynn, B. L. (2018). Lateral, vertical, and longitudinal source area connectivity drive runoff and carbon export across watershed scales. Water Resources Research.

Accepted. We have modified the introduction to highlight the emerging class of spatially distributed observations in the river corridor space and the emergence of new techniques to interpret these data sets. Moreover, we clarify that our data set remains novel because it focused on simultaneous characterization of physical, chemical, and biological systems, spanning the stream water, hyporheic water, and sediment domains (in contrast to past studies that are primarily focused on in-stream water chemistry).

Minor Comments:
Abstract: Is there a reason the authors did not include information from results in the abstract?

Acknowledged. This primary purposes of this manuscript is to document a multi-scale, interdisciplinary data set that is available for the community. Thus, the primary results are the data themselves. We have elected to make no modifications in response to this comment.

P 3 L 11: Replace "who typical" with "who typically"

Accepted. Modified as suggested.

P 3 L 22: Remove " " " between"forests" and "(_400".

Accepted. Modified as suggested.

Section 2.1/Figure 1: How did the authors determine the first order streams? Is this based on the geomorphic channel network, or is this based on permanence of flow? Note: I later saw on P 10 Section 3.1.1. that stream orders were based on a topographic analysis with a 1m DEM (and potentially ground trothed). Please make reference to this earlier.

Accepted. We have added " (see details on network definition in section 3.1.1)." to the caption for Figure 1.

P 4 L 7: Should "term" be capitalized?

Accepted. Modified as suggested.

Figure 1: It is difficult to differentiate the stream orders with the chosen elevation gradient. Perhaps the gradient can be grey scale to help the reader better identify the stream orders?

Acknowledged. Greyscale is already used to represent roadways in the basin, which provide landmarks that link to other studies and maps in the basin. We have elected no modification in response to this comment.

Figure 2: Can the authors please label which of the four catchments represent which of the major landform units within Figure 2? Right now it is unclear which is

which.

Accepted. We have added the following text to the Figure 2 caption: "WS01 and WS03 are located in the Upper Oligocene-Lower Miocene balsaltic flows, Unnamed Creek on a deep-seated earth flow, and Cold Creek in more modern Plieoscascade volcanics. Characteristics of each landform and catchment are detailed in Table 1."

P 10 L 24-29: It is unclear if the drive point piezometers were installed, purged, and hydraulic conductivity was measured all on the same day. If so, I am concerned that the piezometers were not collecting representative hydraulic conductivity values since the piezometers did not have time to "equilibrate" with the natural streambed. Further, if 3-6 replicates of the falling head test were done in sequential order, is it possible that the addition of water into the streambed may create zones of saturation, which may alter the hydraulic conductivity of the subsurface if it was previously dry. Did the authors see trends in the hydraulic conductivity measurements over the 3-6 replicates? If so, this may suggest these replicates were biased and a geometric mean is not the correct way to summarize the results. Honestly, I am surprised the authors could conduct a falling head test in a streambed – this suggests to me that the material below the streambed was dry, or there was perhaps a strong losing gradient.

Acknowledged. Drive point piezometers were installed, purged, and measurements made on the same day. All falling head tests were conducted at locations with flowing surface stream water and were saturated prior to piezometer installation. All hydraulic conductivity replicates are provided in the tabular data for this study, and we do not observe a systematic shift in measurements as replicates proceeded (37 sites with positive trends, 20 sites with negative trends). We did not test the robustness of these trends with any statistical test given the comparable numbers in each direction and the small sample site at each site, but expect none would be statistically significant. Finally, falling head tests in streambeds are a common field technique. For example, see Baxter et al. and more than 200 articles citing this approach.

Baxter, C. V.; Hauer, F.R.; Woessner, W.W. Measuring groundwater-stream water exchange: New techniques for installing minipiezometers and estimating hydraulic conductivity. *Trans. Am. Fish. Soc.* **2003**, *132*, 493–502.

Ultimately, we made no edits in response to this comment.

P11 L 11-12: When where these pots installed? Were the installed during the synoptic sampling campaign, or taken out during the synoptic sampling campaign? This is important information, as 6 weeks is a large portion of the summer and macroinvertebrate communities may shift across these stream orders through the drying down of these river networks.

Accepted. We have added "during the synoptic campaign" to the first sentence of section 3.1.4 to clarify the timing of installation. We also clarified the Surber samples were collected during the synoptic campaign.

P 12 L 5: Rinsing the tubing for 5 minutes with hyporheic water seems like it would greatly alter the hyporheic zone. 5 minutes of pumping at 0.5 L/min suggests that the authors extracted 2.5 L of hyporheic water before sample collection. That suggests the water that was sampled may be from preferential flowpaths that supplied water after the immediate region around piezometer was drained.

Accepted. We agree conceptually with this point. However, we did not control for nor record our flushing rate, though the lead author's recollection of the field campaign is that pumping was slower than the rate cited above. We do note that the sediment is highly porous and conductive, commonly coarse sands and gravels, where the flow disturbance may not be as significant as it would be in less hydraulically conductive material. Since we do not have data to present, we have acknowledged this in the study, adding "We did not record the pumping rates nor volumes for this rinse, and acknowledge it may have impact the flow field prior to sample collection. However, we expect this would be minimal because the sediment is generally highly hydraulically conductive."

P 13 L 12: Potentially missing "and" between "_18O" and "_ 2H".

Accepted. Modified as suggested.

P 13 L 17-20: How quickly after sampling were these samples analyzed? How quickly did it take for samples to "come to room temperature"? Proper superscripts and subscripts needed for the dissolved nutrients.

Accepted. We have modified the text to clarify this point as: Samples were thawed on the laboratory bench prior to analysis (typically 2-4 hours) and were analyzed at room temperature.

P 15 L 6: What are EEA rates? I don't see this defined before in the text.

Accepted. "EEA" replaced with "Extracellular enzymatic activity"

P 18 L 15: Remove second "was" between "was" and "set"

Accepted. Modified as suggested.

P 18 L 16: Potentially missing "." After "co-added"

Accepted. Modified as suggested.

P 20 L 17: replace "valely" with "valley"

Accepted. Modified as suggested.

P 20 L 17: The authors mention "to place both sensors", but what are the sensors used here?

Accepted. "Both sensors" replaced with "two specific conductivity sensors".

P 20 L 20: What is the approximate range of masses of NaCl used for this study? Are the metadata available for these dilution gauging experiments?

Acknowledged. NaCl masses are detailed in the tabular data set associated with this manuscript.

Eric Moore (Referee #2)
eric.m.moore@uconn.edu
Received and published: 7 August 2019
Ward et al. Review
Co-located contemporaneous mapping of morphological hydrological, chemical, and biological conditions in a 5h order mountain stream network, Oregon, USA Ward et al.
Summary: The study involved intensive sampling of 62 field sites during baseflow conditions throughout a 5th order stream network. As noted in the introduction, this was a novel study looking at the interaction of physical, biological, and chemical variables within the river corridor. The authors hosted the data publically to CUAHSI HydroShare which allows open access to the scientific community for use. The authors and other researchers are capable of using the data collected during this study for future analysis, publications, and repeatable studies. These data will be used to look at drivers of river corridor exchange and how they interact spatially throughout a network.

No response to the comments above, as this is a summary of more detailed points that are address individually below as "major comments".

Comments: I'm assuming this is a data release manuscript, but I would like to see a bit more background in the introduction. I think this would help set up the "why" the authors collected the data when and how they collected it.

See response to Referee #1 first major comment.

The Organic Matter Characterization method section gives too much detail and seems out of place with the other method sections. See my suggestions in the line-by-line review below.

See responses to suggested edits for pages 17-19, below.

Line by line review:
Page 1: Good

Off to a strong start just on the cover page and author list!

Page 2: Abstract - The abstract is short and concise but catches all the major topics of the paper

No response necessary.

Lines 26 - 28 - I suggest not having parenthesis in the first sentence of the article. Change the opening line to – River corridor science is the study of the exchange of water, solutes, particulate matter, energy, and biota between surface and subsurface domains, collectively called river corridor exchange.

Accepted. Modified as suggested.

Page 3:
Lines 1 - 2 - Suggestion to switch around co-evolved and known to be tightly coupled. This allows the two co- words to be close together in the sentence and could help the reader understand the point more clearly. First, although the physical, chemical and biological processes are known to be tightly coupled and co-evolved, they are seldom co-investigated.

Accepted. Modified as suggested.

Line 6 - Place the year into the Ward and Packman reference

Accepted. Modified as suggested.

Lines 8 - 11 - Run-on sentence. Suggestion to change to - As a result of these limitations, we currently have only a general understanding of river corridor science exchange processes. This limits our ability to predict these processes or the associated ecosystem functions across spatio-temporal scales relevant to water resource managers and policymakers who typically operate at river network scales.

Accepted. Modified as suggested.

Line 11 - change typical to typically

Accepted. Modified as suggested.

Lines 14 - 17 - Good closing paragraph sentences. The last sentence in starting in line 16 could be bolstered up a little or moved before "Specifically,....". Using this as the last sentence in this paragraph defines the hard cut needed to go into the next section.

Accepted. The sentence in question has been moved before "Specifically…" and now reads "The result is a novel river corridor data set documented herein that presents new opportunities for exploring multi-scale, interacting river corridor patterns and processes."

Line 22 - 23 - Suggestion to change to - Elevation in the basin ranges from 410 to 1630 m, and the landscape is heavily forested with _400 year old Douglas fir trees with areas of younger forest from regrowth or replanting after timber harvest (_400 yr old) is not really necessary if "old growth" is in front of it. I suggest using "including _400 year old Douglas fir forests"...." A.m.s.l (at mean sea level???) I don't think this is necessary

Accepted. We have modified the "old growth" as suggested. We retain "a.m.s.l." (standard abbreviation for above mean sea level) for completeness.

Page 4: Lines 20 - 24 – Split into two sentences All sampling of water and streambed sediment was conducted within the period 26-July through 3-Aug-2016 with no flow or precipitation events recorded during the sampling campaign. All solute tracer experiments occurred during the period 31-July through 12-Aug-2016, again with no recorded flow or precipitation events.

Accepted. Modified as suggested.

Page 5: Figure 1 – remove second synoptic from figure caption

Accepted. Modified as suggested.

Page 6: Figure 2 – Label each landform with a caption above each watershed's figure. There is no way for the reader to know which landform they are looking at.

Accepted. This information has now been added to the figure caption with an explicit cross-reference to Table 1, where details are provided.

Page 7: Table 1 – No need to repeat (HJA, Oregon) if all sampling happened there and it is listed in the table caption prior. I can see how this relates to Figure 2, but it would be great to see the creek names and landform types in Figure 2. This would help related the two figures better

Accepted. We have removed the unnecessary "(HJA, Oregon), and the modifications to the Figure 2 caption now directly link the two elements, and we have added the following text to the table caption: "See catchment topography in Fig. 2 for each site."

Page 8: When printed out the caption of Table 2 appears on it's own page Reduce text size or table size to get Table 2's caption back together with Table 2

Acknowledged. This will be addressed in typesetting of the final article. No modifications made at this time.

Page 9: Table 2: I really like this table! Suggestion to include units within this table to show the wide range of data collected during this experiment. Having the units in the table would allow the reader to see what is comparable right away. See Page 8

comments to get the caption back together with Table 2

Acknowledged. Thanks for a great idea! We did attempt this, but some entries in the table are individual measures (e.g., stream width) while others actually describe a host of related and detailed observations (e.g., FT-ICR-MS). This made it difficult to avoid making a table that got too detailed and unwieldy, so we ultimately retained the form of the initial table.

Page 10: None

☺

Page 11: Lines 19 - 21 – Split this sentence into two sentences

Accepted. Modified as suggested.

Lines 23 - 25 – Plecoptera and Ephemeroptera: : : Family? Genus????

Accepted. "family" and "order" have been added to describe these and Chironomidae.

Page 12: Line 8 – first reference from an instrument company. These references did not appear before this page.

Accepted. We have added documentation of which instrumentation were used to prior locations in the manuscript. Comparable information is now provided throughout the manuscript.

Page 13: None
Page 14: None

Wahoo! Two in a row!

Page 15: Lines 13 -15: Description of sediment analysis method is well done, but what type of analyses were done on the sediment samples. Ash-free dry mass is listed a few paragraphs below, but what other sediment analyses were done?

Accepted. We have added the following text to clarify the fate of these samples: "Samples collected in this fashion were used for extracellular enzymatic activity and FT-ICR-MS analyses, detailed in subsequent sections."

Page 16: Configure Table 3 to fit beneath the paragraph on page 16.
Page 17: Configure Table 3 to fit beneath the paragraph on page 16.

Acknowledged. Page-break issues and layout will be finalized during the production process.

Line 6 – first subheading of the paper? Entire Organic matter characterization section needs to be shortened, cut, and less wordy. The background information from Lines 8 - 13 can all be covered with references.
Page 18: Shorten entire section Lines 9 - 10: write out correct chemical formulae or use chemical names with formulae in a table
Lines 19 - 20: create a table of experimental conditions instead of listing them out. This is very out of place at the end of the paragraph.
Line 25 – what is "the transient"? Definition of (m/z) is not clear when reading further down the page because there are too many acronyms within this section
The suggestion of a table may help the reader keep things straight
Page 19: Shorten section Lines 13 - 16: Table of values would be more clear than writing them out
Page 20: Shorten section. Lines 7 - 10 – Suggestion to remove a sentence that begins with "For example, : : :." This is not a method or needs to be described in a different way

Accepted. The section has been edited to remove extraneous details and streamline for the reader. Overall section 3.3.3 has been reduced by about 50% as a result of these edits.

Line 12 – Valley spelled wrong

Accepted. Modified as suggested.

Page 21: Good
Page 22: Good
Page 23: Good
Page 24: Good
Page 25: Good
Page 26: Good
Page 27: Good

Our best streak yet, albeit mainly the references!

Co-located contemporaneous mapping of morphological, hydrological, chemical, and biological conditions in a 5th order mountain stream network, Oregon, USA

Adam S. Ward[1], Jay P. Zarnetske[2], Viktor Baranov[3,4], Phillip J. Blaen[5,6,7], Nicolai Brekenfeld[5], Rosalie Chu[8], Romain Derelle[9], Jennifer Drummond[5,10], Jan Fleckenstein[11,12], Vanessa Garayburu-Caruso[13], Emily Graham[13], David Hannah[5], Ciaran Harman[14], Jase Hixson[1], Julia L.A. Knapp[15,16], Stefan Krause[5], Marie J. Kurz[11,17], Jörg Lewandowski[18,19], Angang Li[20], Eugènia Martí[10], Melinda Miller[1], Alexander M. Milner[5], Kerry Neil[1], Luisa Orsini[9], Aaron I. Packman[20], Stephen Plont[2,21], Lupita Renteria[22], Kevin Roche[23], Todd Royer[1], Noah M. Schmadel[1,24], Catalina Segura[25], James Stegen[13], Jason Toyoda[8], Jacqueline Wells[22], Nathan I. Wisnoski[26], Steven M. Wondzell[27]

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Abstract. A comprehensive set of measurements and calculated metrics describing physical, chemical, and biological conditions in the river corridor is presented. These data were collected in a catchment-wide, synoptic campaign in Lookout Creek within the H.J. Andrews Experimental Forest (Cascade Mountains, Oregon, USA) in summer 2016 during low discharge conditions. Extensive characterization of 62 sites including surface water, hyporheic water, and streambed sediment was conducted spanning 1st through 5th order reaches in the river network. The objective of the sample design and data acquisition was to generate a novel data set to support scaling of river corridor processes across varying flows and morphologic forms present in a river network. The data are available at http://www.hydroshare.org/resource/f4484e0703f743c696c2e1f209abb842 (Ward, 2019)

1 Introduction

River corridor science is the study of the exchange of water, solutes, particulate matter, energy, and biota between surface and subsurface domains, collectively called river corridor exchange (e.g., Brunke and Gonser, 1997; Boulton et al., 1998; Harvey and Gooseff, 2015; Tonina and Buffington, 2009; Krause et al., 2011, 2017). These beneficial functions are primarily derived from the interactions between physical, chemical, and biological processes in the river corridor (e.g., McDonnell et al., 2007; Boano et al., 2014; Ward, 2015; Bernhardt et al., 2017). In a recent review, Ward (2015) identified

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two key deficiencies that must be addressed to advance our predictive understanding of the functioning of the river corridor. First, although the physical, chemical and biological processes are known to be tightly coupled and co-evolved, they are seldom co-investigated. More comprehensive characterizations of physical-chemical-biological conditions are required to enable the study of coupled processes that span these sub-systems. Second, most comprehensive, interdisciplinary studies are conducted at single locations within an extensive river network and are limited in their range of spatial and temporal scales. Combined, these limitations have hindered our predictive understanding of ecosystem services and functions at the scale of river networks (Ward and Packman, 2018). While interactions between physical, chemical, and biological processes is necessary to improve our predictive understanding at the scale of river networks, this knowledge is not sufficient to achieve that goal.

In addition to local-scale understanding of process interactions and controls, predictive understanding of process dynamics in river networks requires an understanding of spatial structure of processes and their interactions. Traditional studies of river corridors focus on interpretation of time-series analysis of repeated at fixed points. However, an emerging class of data sets and approaches emphasize the value of spatially distributed sampling campaigns in understanding the structure and function of river corridors (e.g., Kaufmann et al. 1991; Wolock et al. 1997; Dent and Grimm, 1999; Temnerud & Bishop 2005; Likens et al, 2006; Hale and Godsey, 2019). Spatially distributed studies along river corridors may provide increased information about biogeochemical processes in comparison to equal effort in characterization of local-scale processes at a size (Lee-Cullin et al., 2018). Similarly, these data sets are driving innovation in the frameworks used to interpret spatially distributed data sets, including foci on spatiotemporal variance (Abbott et al., 2018), the application of geostatistical approaches to characterize scale-dependent relationships linking stream water chemistry and basin characteristics (Zimmer et al., 2013; McGuire et al., 2014; Dupas et al., 2019); and additional spatial statistics methods (Isaak et al., 2014; Lowe et al., 2006).

While each of the studies cited above have made advances, they remain limited in two important dimensions. First, the studies cited above primarily focus on spatial patterns in stream water chemistry with limited characterization of biological and physical dimensions of the river corridor. Second, these studies are almost exclusively focused on measurements in the surface water domain rather than explicitly considering hyporheic waters and the streambed sediments themselves. Consequently, interpretations of causal mechanisms are limited by incomplete characterization and an emphasis on instream water. we have a limited ability to predict river corridor processes and the associated ecosystem functions at the spatio-temporal scales of river networks, where water resource managers and policymakers typically operate (Krause et al., 2011). In response, we endeavored to collect river corridor data that directly address the two limitations by acquiring simultaneous, multidisciplinary measurements distributed across a river network. The result is a novel river corridor data set documented herein that presents new opportunities for exploring multi-scale, interacting river corridor patterns and processes. Specifically, this paper presents the collection of a synoptic-in-time, distributed-in-space characterization of physical,

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Ward and Packman (Accepted) note these two main limitations of previous studies may result in a misattribution of cause and effect because only a subset of the relevant scales and variables are captured in the studies. we

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chemical, and biological conditions in the river corridor of the 5th order Lookout Creek stream network within the H.J. Andrews Experimental Forest and Long Term Ecological Research site (Cascade Mountains, Oregon, USA).

Moved up [1]: This data set presents new opportunities for exploring multi-scale, interacting river corridor patterns and processes.¶

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2. Study location and campaign design

2.1 Study catchment

The H.J. Andrews Experimental Forest (HJA) is a 5th order catchment draining about 6,400 ha. The forest is located in the Western Cascades, Oregon, USA. Elevation in the basin ranges from about 410 to 1,630 m a.m.s.l., and the landscape is heavily forested, including 400-yr old Douglas fir forests and areas of younger regrowth forest after wildfire or was replanted after forest harvest. Additional detail about the climate, morphology, geology, and ecology of the site and region are well described by others (Dyrness, 1969; Swanson and James, 1975; Swanson and Jones, 2002; Jefferson et al., 2004; Deligne et al., 2017).

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Within the study catchment, there are three predominant landforms (Table 1; Figs. 1, 2). First, lower elevations are typically underlain by thermally weakened Upper Oligocene - Lower Miocene basaltic flows. These landforms are typified by highly dissected landscapes resulting from rapidly incising v-shaped valleys that are steep and narrow, with colluvium emplaced by high energy hillslope failures and debris flows. Second, high elevations are typically underlain by plieocascade volcanics. These higher-elevations have well-defined, u-shaped valleys resulting from glacial processes, with cirques at the head of valleys and highly compacted glacial tills filling the valley bottoms. Third, several deep seated earth flows are emplaced on the Upper Oligocene - Lower Miocene basaltic flows. These earth flow landforms typically lack well developed drainage networks, because they are too young to have developed large valleys and thus have minimal lateral constraint or visible bedrock along the streams.

The HJA has been the site of forest management, watershed and ecosystem research since it was established as a U.S. Forest Service research site in 1948, and has been one of the National Science Foundation's Long-term Ecological Research sites since 1980. As a result of these efforts and sustained commitment to data stewardship, the HJA hosts an extensive catalogue of data, maps, images, models, and software that are complementary to the data presented in this publication and provide context within which these data can be interpreted (see HJA Data catalog at https://andrewsforest.oregonstate.edu/data). For example, there are many complementary datasets of interest to readers of this manuscript, including stream discharge (HF004), stream chemistry (CF002), meteorological data (MS001), precipitation and dry deposition chemistry (CP002), aquatic invertebrate inventories (SA012, SA013, SA017), and soil properties and chemistry (SP001, SP006, SP026). We note these data are only a subset of the available information and encourage users of the data to explore the HJA data catalogue for additional information.

2.2 Synoptic campaign design

This study was designed to replicate characterizations of the river corridor at a total of 62 sites spanning 1st through 5th order reaches in the HJA. Site selection was based on (1) the presence of flowing surface waters; (2) stratification across stream orders; (3) coverage of the three major landform units in the HJA; and (4) accessibility of sites. All sampling of water and streambed sediment was conducted within the period 26-July through 3-Aug-2016 with no flow or precipitation events recorded during the sampling campaign. All solute tracer experiments occurred during the period 31-July through 12-Aug-2016, again with no recorded flow or precipitation events.

Deleted: All sampling of water and streambed sediment was conducted within the period 26-July through 3-Aug-2016 with no flow or precipitation events recorded during the sampling campaign, and all solute tracer experiments during the period 31-July through 12-Aug-2016 (again with no recorded flow or precipitation events).¶

In addition to broad spatial coverage of the river network, we selected 4 subcatchments for a more detailed characterization consisting of replication along the study reach at 4 to 6 locations per subcatchment. These 4 subcatchments were selected to have one subcatchment in the 3 predominant landforms in the study catchment, plus a fourth subcatchment located where a large debris flow scoured a section of the river corridor to bedrock in 1996 (Johnson, 2004). The objective of including 2 subcatchments in the low-elevation landform, was to provide a space-for-time comparison (i.e., WS01 and WS03 provide two realizations of the same landform type at different states in response to the large debris flow that typifies a key geologic disturbance in the system).

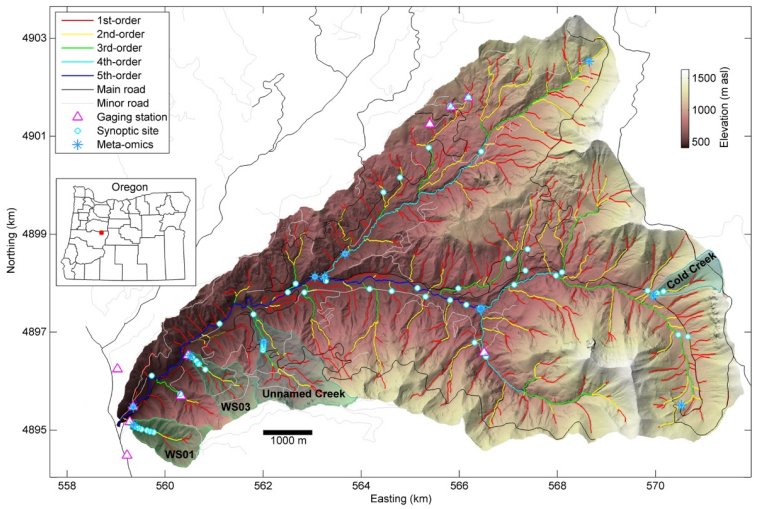

Figure 1. Synoptic sites and LiDAR-derived stream network (see details on network definition in section 3.1.1).

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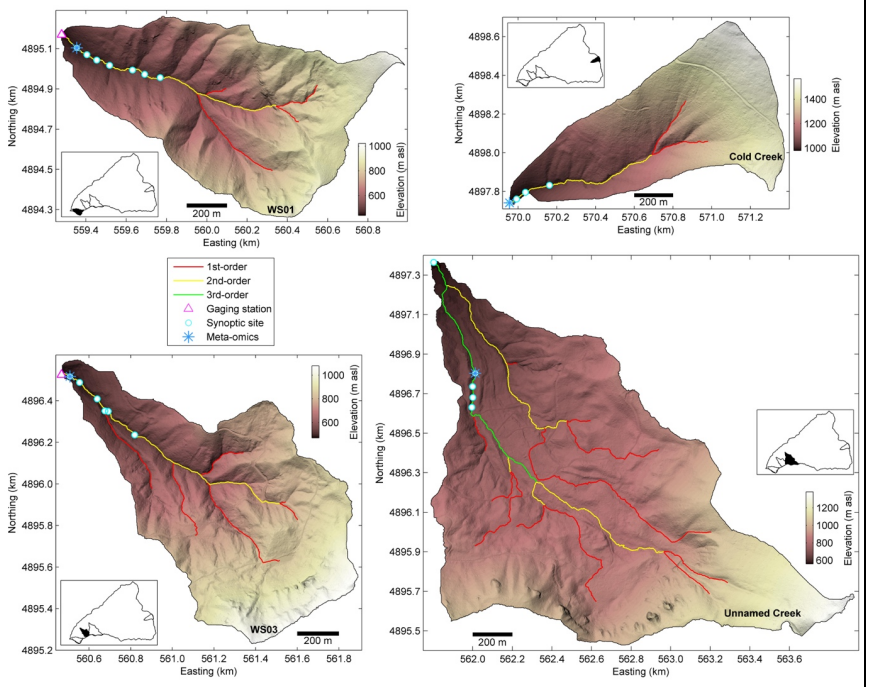

Figure 2. Headwater catchments in the major landform units at the H.J. Andrews Experimental Forest, including multiple synoptic sites along an intensively studied reach. **WS01 and WS03 are located in the Upper Oligocene-Lower Miocene balsaltic flows, Unnamed Creek on a deep-seated earth flow, and Cold Creek in more modern Plieoscascade volcanics. Characteristics of each landform and catchment are detailed in Table 1.**

Table 1. Summary of site characteristics for the 4 headwater catchments where more intensive sampling was conducted. The descriptions of these headwater catchments are considered representative of the major landform types within the HJA [after Dyrness, 1969; Swanson and James, 1975; Swanson and Jones, 2002]. See catchment topography in Fig. 2 for each site.

Site	Study Reach	Geologic Setting	Valley form	Colluvium presence and description	Notable river corridor description	Constraint	Lateral Inflows	Spatially Intermittant?
WS01	Lower	Upper Oligocene - Lower Miocene Basaltic Flows, Volcanoclastic Rocks. Thermally altered (weakened) by subsequent volcanic activity enabling rapid downcutting of the valley bottoms.	V-shaped valley w/ Wide (10-20-m) valley bottom	Inceptisols. Abundant deposition from hillslope debris flows. Highly porous. Minimally compacted.	Pool-riffle-step and Pool-step-riffle morphology. Channel splits. Gravel wedges. Long, continuous sections of deposition from high-energy debris flow events.	Observed lateral (valley walls) and vertical (streambed) constraint of active channel	Proportional to lateral tributary area of hillslopes. Hillslopes underlain by intact bedrock.	Yes. Diurnal fluctuations in stream discharge enable rapid shift from continuous to intermittant over repeated 24-hr cycles.
	Middle							
	Upper							
WS03	Lower		V-shaped valley w/ Narrow (2-10 m) valley bottom	Deposition of colluvium from 1996 scouring event				Yes
	Middle			Intermittant inceptisol-based colluvium on bedrock	Isolated gravel wedges formed by large woody debris			Yes, below features
	Upper			Minimal colluvium present	100% Surface Flow (no colluvium)			No
Unnamed Creek	Upper	Deep-seated earth failure on Upper Oligocene - Lower Miocene Basaltic Flows	Early downcutting & valley formation in unstructure colluvial material	Extensive colluvium. Flat and wide valley bottom with lateral meandering of active channel in incising valley bottom	Meanders, cut banks more typical of alluvial valleys compared to other study catchments proposed	No visible bedrock in active channel	No known groundwater nor lateral inflows. Minimal lateral tributary area in study reach	Unknown at this time. Expected due to the site of colluvial deposit.
	Lower							
Cold Creek	Upper	Plieocascase volcanics atop Middle and Upper Miocene Volcanics (Andesite, Basalt)	U-shaped valley (glacial cirque)	Compacted glacial tills	Large woody debris on till forms pools, steps with intermediate graveland cobble riffles	Bedrock visible at 1 location	Proportional to hillslope area	Unknown at this time. Not expected given apparent contributions from aqufier.
	Lower						Aquifer extends beyond catchment	

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Site	Study Reach	Geologic Setting	Valley form	Colluvium presc and descripti
WS01 (HJA, Oregon)	Lower	Upper Oligocene - Lower Miocene Basaltic Flows, Volcanoclastic Rocks. Thermally altered (weakened) by subsequent volcanic activity enabling rapid downcutting of the valley bottoms.	V-shaped valley w/ Wide (10-20-m) valley bottom	Inceptisols. Abur deposition fro hillslope debris f Highly porou Minimally compa
	Middle			
	Upper			
WS03 (HJA, Oregon)	Lower		V-shaped valley w/ Narrow (2-10 m) valley bottom	Deposition of coll from 1996 scou event
	Middle			Intermittant incep based colluviun bedrock
	Upper			Minimal colluvi present
Kerry Creek (HJA, Oregon)	Upper	Deep-seated earth failure on Upper Oligocene - Lower Miocene Basaltic Flows	Early downcutting & valley formation in unstructure colluvial material	Extensive colluv Flat and wide v bottom with lat meandering of a channel in incis valley bottor
	Lower			
Cold Creek (HJA, Oregon)	Upper	Plieocascase volcanics atop Middle and Upper Miocene Volcanics (Andesite, Basalt)	U-shaped valley (glacial cirque)	Compacted glaci
	Lower			

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Table 2. Left: Summary of sample collection (site characterization, streambed sediment, stream water, hyporheic water) and analyses included in this data set. Center: mapping of data types to their characterization of physical, chemical, and/or biological systems (after definitions of Ward, 2015). Right: data archival summary

	Sample Location				System(s)			
	Site	Surface Water	Hyporheic Water	Streambed Sediment	Physical	Chemical	Biological	Data location
Drainage area	■				■			Tabular, Network Geometry
Valley slope	■				■			Tabular, Network Geometry
Valley width	■				■			Tabular, Network Geometry
Stream slope	■				■			Tabular, Network Geometry
Stream width, depth	■				■			Tabular
Stream order	■				■			Tabular, Network Geometry
Sinuosity	■				■			Tabular, Network Geometry
Discharge	■				■			Tabular
Site Coordinates	■				■			Tabular
Temperature		■	■		■	■		Tabular
Specific conductivity		■	■		■	■		Tabular
^{2}H, ^{18}O water isotopes		■	■		■	■		Tabular
Hydraulic Conductivity				■	■			Tabular
DO		■	■			■	■	Tabular
NPOC		■	■			■	■	Tabular
SUVA254		■	■			■	■	Tabular
Spectral slope ratio		■	■			■	■	Tabular
TDN		■	■			■	■	Tabular
DOM EEMs		■	■			■	■	Tabular
Fluorescence Index		■	■			■	■	Tabular
Anions (Cl, SO4)		■	■			■	■	Tabular
Cations (Na, K, Mg, Ca)		■	■			■	■	Tabular
NO2+NO3		■	■			■	■	Tabular
PO4		■	■			■	■	Tabular
NH3		■	■			■	■	Tabular
Macroinvertebrate Community		■		■			■	Tabular
Extracellular Enzymatic Activity (N, P, C acquiring)				■		■	■	Tabular
% Organic Matter				■	■	■	■	Tabular
Stream solute tracer	■				■			Solute Tracers
FT-ICR-MS				■		■	■	FTICRMS
16S DNA		■	■	■			■	NCIB

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	Sample Location			
	Site	Surface Water	Hyporheic Water	Streambed Sediment
Drainage area	■			
Valley slope	■			
Valley width	■			
Stream slope	■			
Stream width, depth	■			
Stream order	■			
Sinuosity	■			
Discharge	■			
Net gaining/losing	■			
Site Coordinates	■			
Temperature		■	■	
Specific conductivity		■	■	
2H, 18O water isotopes		■	■	
Hydraulic Conductivity				■
Grain size distirbution				■
DO		■	■	
NPOC		■	■	
SUVA254		■	■	
Spectral slope ratio		■	■	
TDN		■	■	
DOM EEMs		■	■	
Fluorescence Index		■	■	
Anions (Cl, SO4)		■	■	
Cations (Na, K, Mg, Ca)		■	■	
NO2+NO3		■	■	
PO4		■	■	
NH3		■	■	
Macroinvertebrate Community		■		■
EEA (N, P, C acquiring)				■
% Organic Matter				■
Stream solute tracer	■			
FT-ICR-MS				■
16S Diversity DNA		■	■	■

3. Methods

3.1 Synoptic Site Characterization

3.1.1 Topographic Analysis

The stream network was derived from a 1-m digital terrain model based on airborne LiDAR collected in 2008 (Spies, 2018). We used the one-directional flow accumulation algorithm (Seibert and McGlynn, 2007) implemented in a modified version of TopoToolbox (Schwanghart and Kuhn, 2010; Schwanghart and Scherler, 2014) to derive the direction of flow and accumulation of drainage area within the basin. We defined the stream network as any location draining more than 5 ha. The threshold was established based on iteratively comparing the derived stream network to our experience working in headwater catchments and their extent (consistent with analyses by Ward et al., 2018). The TopoToolbox algorithm defined study reaches as the segment between two junctions. In our analysis, we defined 686 river corridor segments including a total length of about 209 km of valley containing about 242 km of stream. For each study reach, we tabulated the sinuosity of the stream within the valley. Next, we discretized each reach into 10-m segments, extracting valley slope, stream sinuosity, and stream slope for each segment (after Corson-Rikert et al., 2016; Ward et al., 2018). Each synoptic site was assigned a stream order and average valley slope, streambed slope, and sinuosity for the reach within which it was located.

3.1.2 Hydraulic and valley geometry

At each synoptic site, field observations of valley width were collected using a tape measure, with valley edge being visually defined in the field based on the hillslope break-point between the relatively flat valley bottom and steeper valley walls. Total wetted channel width was measured perpendicular to the direction of flow at the synoptic site, and average channel depth was recorded based on at least five measurements of depth spaced evenly across the channel.

3.1.3 Hydraulic conductivity

At the approximate centerline of the synoptic site, a Solinst 615N drive-point piezometer (615N, Solinst Canada, Ltd., Georgetown, ON, Canada) was driven to a depth of about 65-cm below the streambed. The piezometer was screened over the distance of 50-65-cm below the streambed. The piezometer was developed and purged by pumping slowly using a peristaltic pump until the water was visually clear, typically about 5 minutes. Then hyporheic water sampling occurred as described below (Section 3.2). Then a series of 3-6 replicates of a falling head test were conducted using the piezometer, with water levels measured using a Van-Essen MicroDiver (DI601, Van Essen Instruments, Mukilteo, WA, USA), recording at 0.5-s intervals and corrected for any variation in atmospheric pressure collecting data every 10-min. Falling

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head data were used to estimate hydraulic conductivity after Hvorslev (1951). We report the geometric mean of the replicate tests for each synoptic site. Finally, we note that at 5 sites there was minimal (~<10cm) to no colluvium present in the valley bottom. At these sites we did not sample hyporheic water nor measure hydraulic conductivity, but we did collect streambed sediment from small in-channel deposits at the synoptic site. These sites are necessary for complete representation of the river corridor of the study catchment as there are many locations in the valley bottom that have minimal or no colluvium..

3.1.4 Macroinvertebrate community

Benthic macroinvertebrate colonization pots were installed at 44 of the 62 synoptic sites using the design of Crossman et al. (2012) during the synoptic campaign. Colonization pots were constructed of wire mesh with 1.25 cm openings formed into cylinders approximately 15-cm in height and 8-cm in diameter, including a screened bottom. Hence, at sites where surface sediment grain sizes were larger than 8-cm, they could not be installed. Substrate was excavated by hand and placed in each pot prior to installing so that the top of each pot was level with the streambed. Colonization pots remained in situ for about 6 weeks following installation. Removal was achieved by pulling a cable to raise a specially constructed tarpaulin bag around the sides of the pot before extraction, thereby minimizing sample loss. All substrate and macroinvertebrates were placed in a 90% ethanol solution for preservation. Additionally at 10 sites, surface samples of macroinvertebrates were collected with a Surber sampler with a 330 micron mesh net, collected in triplicate at proximal locations and pooled for identification during the synoptic campaign. Surface samples were processed using identical preservation methods; and identification was conducted by the same researcher.

After separation of macroinvertebrates, sediment samples were oven dried and sieved to assemble grain size distributions for each colonization pot. Importantly, because the pots were packed by hand in flowing water, we expect these grain size distributions are biased toward the coarse fraction of streambed sediment, as finer materials would have washed away during packing. Additionally, large cobbles would not have fit into the pots and excluded from collection.

Identification was performed under the stereomicroscope, except for the Chironomidae (family larvae and early larval instars of the Plecoptera (order) and Ephemeroptera (order), which were mounted in the Euparal and examined under the light microscope as described by Andersen (2013). Macroinvertebrates were identified to the lowest possible taxonomic level, including the differentiation of adult and juvenile stages. Identification was performed using established keys (Merritt & Cummins, 1996; Andersen, 2013; Malicky, 1983; Langton, 1991; Epler, 2001).

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3.2 Water sampling & analyses

3.2.1 Sample collection from stream and hyporheic zone

All water samples were collected using a peristaltic pump to sample water at a flow rate of about 0.5 L/min. The pump intake was located either in the stream thalweg for surface samples or in the developed piezometer for hyporheic samples. Tubing was rinsed with water from the stream or hyporheic zone for at least 5 minutes prior to sample collection to minimize cross-contamination between sites. We did not record the pumping rates nor volumes for this rinse, and acknowledge it may have impact the flow field prior to sample collection. However, we expect this would be minimal because the sediment is generally highly hydraulically conductive.

First, water temperature and dissolved oxygen were recorded using a YSI ProODO handheld probe (YSI, Inc., Yellow Springs, OH, USA) with an optical dissolved oxygen (DO) sensor and thermistor. For stream samples, the probe was held in the water column at the synoptic site near the pump intake.. For hyporheic samples, water was pumped into a small flow-through cell until it overflowed, and then the sensor placed into cell while flow continued. For both stream and hyporheic observations the sensor remained in place in the flowing water until probe readings for temperature and DO stabilized. Specific conductivity was also measured with a handheld conductivity probe (YSI EC300; YSI, Inc., Yellow Springs, OH, USA) using the same approaches.

Physical water samples for subsequent laboratory analyses were collected from the stream and hyporheic zone using identical methods, including: (1) Unfiltered samples for water isotope analysis (Section 3.2.2) were collected in 20 mL glass scintillation vials with conical inserts and were capped without headspace to minimize fractionation. (2) Samples for dissolved water chemistry and nutrients (Section 3.2.3) were collected by field filtering using handheld 65 mL syringes. Syringes were triple rinsed with sample water prior to collection of any sample volume. Samples for dissolved organic carbon (DOC) analyses were field-filtered using a 0.2 µm cellulose acetate filter. Acid-washed amber HDPE bottles were triple-rinsed with filtered sample water prior to sample collection. DOC samples were placed in a cooler with ice in the field and remained chilled until analysis. Samples for dissolved nutrients, anions, and cations were field-filtered using a 0.45 µm cellulose acetate filter. Sample bottles were triple-rinsed with filtered sample water prior to sample collection. Dissolved nutrient samples were placed on dry ice in the field immediately after collection and remained frozen until analysis. (3) Samples for microbial analysis (Section 3.2.4) were collected following Crevecoeur et al. (2015) by pumping water through a Sterivex (Millipore) cartridge with a 0.22 µm Durapore (PVDF) filter membrane until either 1 L of water was filtered or 45 minutes elapsed. Cartridges were immediately sparged to remove site water, filled with RNAlater stabilization solution (Ambion), and frozen in the field on dry ice. Samples remained frozen on dry ice until transferred and stored in a -80 °C freezer until analysis.

3.2.2 Water stable isotopes ratios

We analyzed water stable isotopes to facilitate characterization of water ages using a cavity ring down spectroscopy method (Picarro L2130-I, Picarro Inc.), following laboratory protocols described by Nickolas et al. (2017). Briefly, samples were run under high-precision analysis mode using a 10 µL syringe for six injections per sample. We discarded the first three injections to eliminate memory effects. We used internal standards to develop calibration equations for stable isotopes of oxygen and hydrogen. The internal standards were calibrated using primary IAEA standards for Vienna Standard Mean Ocean Water (VSMOW2: δ18O = 0.0‰, δ2H = 0.0‰), Standard Light Antarctic Precipitation (SLAP2: $\delta^{18}O$ = −55.5‰, $\delta^{2}H$ = −427.5‰), and Greenland Ice Sheet Precipitation (GIPS: δ18O = −24.76‰, δ2H = −189.5‰). All stable isotopic values were reported as delta (δ) values in parts per thousand (‰), which represent the deviation from the adopted VSMOW2 standard. Internal laboratory precision of the mean reported $\delta^{18}O$ and $\delta^{2}H$ values was estimated as 0.03‰ and 0.058‰ for $\delta^{18}O$ and $\delta^{2}H$ respectively based on the analysis of >50 duplicate samples. The external accuracy - representing the overall accuracy of the laboratory - was estimated as 0.058‰ and 0.241‰ for $\delta^{18}O$ and $\delta^{2}H$ by comparing >60 estimated values for a known standard. A total of 7 samples collected for water isotope analysis were lost due to breakage of collection vials during transport. Paired surface- and hyporheic samples were re-collected on 1-3 August 2016 for these locations.

3.2.3 Dissolved water chemistry and nutrients

Dissolved nutrients PO_4^{3-}, NO_2^{-}+NO_3^{-}, and NH_3 were analyzed on a San++ Automated Wet Chemistry Analyzer - Segmented Flow Analyzer (Skalar Analytical B.V., Netherlands). Anions (Cl^{-}, SO_4^{2-}) and cations (Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}) were analyzed on a Dionex ICS5000 ion chromatography system (Thermo Fisher Scientific). Samples were thawed on the laboratory bench prior to analysis (typically 2-4 hours) and were analyzed at room temperature.

DOC concentrations (as non-purgeable organic carbon, NPOC) and total dissolved nitrogen (TDN) were analyzed via acid-catalyzed high temperature combustion using a Shimadzu TOC-L Analyzer with a TN module (Shimadzu Scientific Instruments, Kyoto, Japan). Samples were allowed to come to room temperature prior to analysis.

Dissolved organic matter (DOM) optical quality was analyzed via absorbance and fluorescence spectroscopy. UV-visible absorbance spectra ranging from 220 to 800 nm were collected using semi-micro, Brand-Tech cuvettes with a 1-cm path length on a Shimadzu dual-beam UV 1800 spectrophotometer (Shimadzu Scientific Instruments, Kyoto, Japan). Samples were allowed to come to room temperature prior to analyses. EPure water (18 MΩ, Barnstead EPure system) as a blank and cuvettes were triplicate rinsed with Epure water and rinsed with sample water between readings.

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Excitation-Emission Matrices (EEMs) were measured over excitation wavelengths of 250-450 nm and emission wavelengths of 320-550 nm on a Horiba Aqualog Fluorometer (Horiba Scientific, Kyoto, Japan). Following the methods of Cory et al. (2010b), EEMs were generated for each sample using a 4 second integration time using a quartz cuvette with a 1-cm path length and Epure water as a blank. Samples were allowed to come to room temperature prior to analysis. Cuvettes were rinsed with Epure water at least 10 times and triplicate rinsed with sample water between readings. EEMs were corrected for instrument-specific excitation and emission corrections and the inner-filter effect (Cory et al., 2010b). Epure water blank EEMs were collected and used to correct for Raman scattering. Fluorescence intensities from corrected-sample EEMs were converted to Raman units (Stedmon and Bro, 2008). EEMs corrections and processing were performed using Matlab consistent with Cory et al. (2010b).

Using EEMs and UV-visible absorbance spectra, several DOM quality indices were calculated for each sample. Specific UV absorbance at 254 nm (SUVA254) was calculated using absorbance readings at 254 nm normalized for path length (in m^{-1}) and DOC concentration (in mg L-1). Higher SUVA254 values are associated with higher aromaticity of DOM (Weishaar et al., 2003). Spectral slope ratio (SR) was calculated from absorbance spectra following the methods of Helms et al. (2008). SR values correspond inversely to relative DOM molecular weight. Fluorescence Index (FI) was calculated following Cory and McKnight (2005) as the ratio of emission (em) intensities for 470 nm and 520 nm at the 370 nm excitation (ex) wavelength. FI values correspond to DOM source with lower FI values corresponding to allochthonous, terrestrially-derived DOM and higher FI values corresponding to autochthonous, microbially-derived DOM (McKnight et al., 2001).

Intensities of specific EEMs peaks and absorbance wavelengths were selected and reported as well-documented proxies for character and sources of DOM. Following Coble (1996) and Cory and Kaplan (2012), EEMs peak A (ex 250, 420/em 500) and peak C (ex 250, 365/em 466) were reported as proxies for humic-like, terrestrially-derived fluorescent DOM (FDOM). EEMs peak T (ex 250, 285/em 344) was reported as a proxy for protein-like FDOM (Cory and Kaplan, 2012). Specific decadic and Naperian absorption coefficients reported serve as proxies for colored DOM (CDOM), and can be used as indicators for specific sources and reactive fractions of the DOM pool (Spencer et al., 2009b). Decadic absorption coefficients (in m^{-1}) were calculated from absorbance readings at specific wavelengths normalized for path length (in m). Naperian absorption coefficients (in m^{-1}) are reported on a natural log scale and are calculated from absorbance readings at specific wavelengths normalized for path length (in m) and multiplied by a factor of 2.303.

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3.2.4 Microbial ecology

To characterize the bacterial communities collected from the surface water and hyporheic zone, we first isolated the filter membrane from the Sterivex cartridge. We extracted DNA from the filters using the DNeasy PowerWater kit (Qiagen). Following DNA extractions, we used PCR to amplify the V4-V5 region of the 16S rRNA gene using barcoded primers (515F and 806R) designed for the Illumina MiSeq sequencing platform (Caporaso et al. 2012). The sequence libraries were cleaned using the AMPure XP purification kit (Agencourt) and quantified using the PicoGreen dsDNA quantification kit (Quant-iT, Invitrogen). Libraries were pooled at 10 ng per library. Pooled DNA and Total RNA libraries were sequenced on the Illumina MiSeq platform at the Center for Genomics and Bioinformatics sequencing facility at Indiana University using paired-end reads (Illumina Reagent Kit v2, 500-reaction kit).

3.3 Sediment sampling & analyses

3.3.1 Sample collection

Streambed sediment samples were collected near the piezometer at each synoptic site. Sample collection involved manually removing the armor layer from the bed and then using a small specimen cup and putty knife to remove bed sediment without loss of fines. Samples were sieved to remove coarse material using a 2-mm sieve. Sieved material was placed in a sterile 50-mL centrifuge tube and frozen on dry ice immediately after collection. Samples were retained on dry ice or in a -80 °C freezer until analysis. Duplicate sediment samples were collected for analysis of extracellular enzymatic activity at 9 sites. Samples collected in this fashion were used for extracellular enzymatic activity and FT-ICR-MS analyses, detailed in subsequent sections.

3.3.2 Extracellular Enzymatic Activity

Enzyme activities were determined using laboratory assays in which sediment extracts were exposed to model substrates that are hydrolyzed by the enzymes (Table 3). Protocols were based on those described by Sinsabaugh et al. (1997) and Belanger et al. (1997). Frozen sediment samples were thawed to room temperature and then 10 mL of 5-mM sodium bicarbonate buffer solution was added to approximately 1 mL subsamples of sediment in 15-mL centrifuge tubes. These tubes were homogenized with a vortex mixer for 15 s and then centrifuged for 15 min at 400 g. Samples were then stored in a refrigerator overnight and the following day 200 µL of the supernatant was pipetted in triplicate onto 96-well microplates. To ensure that any increase in fluorescence was due to enzyme activity, a set of control samples which had been boiled for 5

minutes to denature enzymes was also added to the plates. A set of standard solutions with known concentrations of fluorescent product were also added to each plate to generate a standard curve.

Background fluorescence readings were recorded and substrate solution was added to start the enzyme reaction. Each well in the microplate received 50 µL of a 200 µM substrate solution. Fluorescence measurements (440-nm emission intensity and 365-nm excitation wavelength) were recorded every ~30 min for at least 3 h. Microplates were protected from light and kept at room temperature between readings. Fluorescence was measured using a BioTek Synergy Mx microplate reader. The accumulation of fluorescent products (AMC or MUF, see Table 2) from the hydrolysis reactions was measured over time and enzyme activity was calculated as the slope of a regression of AMC or MUF concentration against time.

About 1 mL of each sediment sample was dried, weighed, and then combusted at 550 °C and re-weighed to determine ash-free dry mass (AFDM) and percent organic content for the sample (Wallace et al. 2006). Extracellular enzymatic activity rates were then normalized to organic matter content and are reported in units of µmol g $AFDM^{-1}$ h^{-1}.

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Table 3. Enzymes examined in this study and the reactions they catalyze.

Enzyme	Model Substrate	Product	Reaction
β-D-glucosidase (GLU)	4-MUF-β-D-glucopyranoside	MUF[1]	Hydrolysis of glucose from cellobiose and cellulose
Alkaline phosphatase (AP)	4-MUF-phosphate	MUF[1]	Hydrolysis of phosphate from phosphosaccarides and phospholipids
Leucine aminopeptidase (LAP)	L-Leucine -AMC	AMC[2]	Hydrolysis of leucine from polypeptides
N-acetylglucosaminidase (NAG)	MUF-N-acetyl-β -D-glucosaminide	MUF[1]	Degradation of chitin and other β-1,4-linked glucosamine polymers

1 MUF = 4-methylumbelliferyl
2 AMC = 7-amino-4-methylcoumarin

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3.3.3 Organic matter characterization

FT-ICR-MS solvent extraction and data acquisition

We performed Electrospray ionization (ESI) and Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry (MS) using a 12 Tesla Bruker SolariX FT-ICR-MS located at the Environmental Molecular Sciences Laboratory (EMSL) in Richland, WA, USA. Prior to mass spectrometry, organic matter was extracted from sediments by adding 1 ml of water (18MΩ ionic purity) to 500 mg of sediments (after Tfaily et al. 2017). Each sediment sample was extracted 3x with the above procedure. Supernatant from all extractions were combined and diluted to 5 mL to generate a final aliquot for analysis. These aliquots were acidified to pH 2 with 85% phosphoric acid and extracted with PPL cartridges (Bond Elut), following Dittmar et al. (2008). We performed weekly calibration after Tfaily et al. (2017) and instrument settings were optimized using Suwannee River Fulvic Acid (IHSS). The instrument was flushed between samples using a mixture of water and methanol. Blanks were analyzed at the beginning and the end of the day to monitor for background contaminants.

Samples were injected directly into the mass spectrometer and the ion accumulation time was set to 0.1s . Data were collected from 98 – 900 m/z at 4M, yielding 144 scans that were co-added. A standard Bruker ESI source was used to generate negatively charged molecular ions. Samples were introduced to the ESI source equipped with a fused silica tube (30 µm i.d.) through an Agilent 1200 series pump (Agilent Technologies) at a flow rate of 3.0 µL min-1. Experimental conditions were as follows: needle voltage, +4.4 kV; Q1 set to 50 m/z; and the heated resistively coated glass capillary operated at 180 °C.

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Deleted: to infer differences in metabolites among our samples. ESI FT-ICR-MS has emerged as a robust method for determining the chemistry of natural organic compounds (Kim et al., 2003; Koch et al., 2005; Tremblay et al., 2007; Tfaily et al., 2011). ESI FT-ICR-MS has been used to distinguish metabolites among ecosystems and soil types (Tfaily et al., 2015; Tfaily et al., 2017) as well as to provide information on the utilization of distinct metabolites among samples within a single environment (Bailey et al., 2017; Graham et al., 2017; Stegen et al., 2018).¶
¶
Ultra-high resolution mass spectrometry of each sample was carried out using a 12 Tesla Bruker SolariX FT-ICR-MS located at the
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Deleted: Samples were removed from the shaker and left to stand before centrifugation at 2000 rpm for 10 min. The supernatant from each sample extraction was removed. Each sediment sample was
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Deleted: using a tuning solution containing C2F3O2, C6HF9N3O, C12HF21N3O, C20H18F27N3O8P3, and C26H18F39N3O8P3 with mass-to-charge ratios (m/z) ranging from 112 to 1333 (Agilent Technologies, Santa Clara, CA USA), and instrument settings
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FT-ICR-MS data processing

One hundred forty-four individual scans were averaged for each sample and internally calibrated using an organic matter homologous series separated by 14 Da (–CH2 groups). The mass measurement accuracy was less than 1 ppm for singly charged ions across a broad m/z range (100-1200 m/z). The mass resolution was ~240K at 341 m/z. The transient was 0.8 seconds. Data Analysis software (BrukerDaltonik version 4.2) was used to convert raw spectra to a list of m/z values applying FTMS peak picker module with a signal-to-noise ratio (S/N) threshold set to 7 and absolute intensity threshold to the default value of 100. Peaks were treated as presence/absence data because peak intensity differences are reflective of ionization efficiency as well as relative abundance (Kujawinski and Behn, 2006; Minor et al., 2012; Tfaily et al., 2015; Tfaily et al., 2017).

Putative chemical formulae were then assigned using in-house software following the Compound Identification Algorithm (CIA), proposed by Kujawinski and Behn (2006), modified by Minor et al. (2012), and previously described in Tfaily et al. (2017). Chemical formulae were assigned based on the following criteria: S/N >7, and mass measurement error <1 ppm, taking into consideration the presence of C, H, O, N, S and P and excluding other elements. To ensure consistent formula assignment, we aligned all sample peak lists for the entire dataset to each other in order to facilitate consistent peak assignments and eliminate possible mass shifts that would impact formula assignment. We implemented the following rules to further ensure consistent formula assignment: (1) we consistently picked the formula with the lowest error and with the lowest number of heteroatoms and (2) the assignment of one phosphorus atom requires the presence of at least four oxygen atoms.

The chemical character of thousands of peaks in each sample's ESI FT-ICR-MS spectrum was evaluated on van Krevelen diagrams. Compounds were plotted on the van Krevelen diagram on the basis of their molar H:C ratios (y-axis) and molar O:C ratios (x-axis) (Kim et al., 2003). Van Krevelen diagrams provide a means to visualize and compare the average properties of organic compounds and assign compounds to the major biochemical classes (e.g., lipid-, protein-, lignin-, carbohydrate-, and condensed aromatic-like). In this study, biochemical compound classes are reported as relative abundance values based on counts of C, H, and O for the following H:C and O:C ranges; lipids ($0 < O:C \leq 0.3$, $1.5 \leq H:C \leq 2.5$), unsaturated hydrocarbons ($0 \leq O:C \leq 0.125$, $0.8 \leq H:C < 2.5$), proteins ($0.3 < O:C \leq 0.55$, $1.5 \leq H:C \leq 2.3$), amino sugars ($0.55 < O:C \leq 0.7$, $1.5 \leq H:C \leq 2.2$), lignin ($0.125 < O:C \leq 0.65$, $0.8 \leq H:C < 1.5$), tannins ($0.65 < O:C \leq 1.1$, $0.8 \leq H:C < 1.5$), and condensed hydrocarbons ($0 \leq 200$ $O:C \leq 0.95$, $0.2 \leq H:C < 0.8$) (Tfaily et al., 2015).

Finally, we calculated the Gibbs Free Energy of OC oxidation under standard conditions (ΔGoCox) from the Nominal Oxidation State of Carbon (NOSC) after La Rowe and Van Cappellen (2011). Though the exact calculation of ΔGoCox necessitates an accurate quantification of all species involved in every chemical reaction in a sample, the use of NOSC as a

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Deleted: NOSC was calculated from the number of electrons transferred in OC oxidation half reactions and is defined by the equation:¶

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→NOSC = -((-Z +4a +b -3c-2d+5e-2f)/a) + 4¶

¶

where a, b, c, d, e, and f are, respectively, the numbers of C, H, N, O, P, S atoms in a given organic molecule and Z is net charge of the organic molecule (assumed to be 1). In turn, ΔGoCox was estimated from NOSC following La Rowe and Van Cappellen (2011):¶

¶

→ΔGoCox = 60.3 – 28.5(NOSC)¶

¶

Values of ΔGoCox are generally positive, indicating that OC oxidation must be coupled to the reduction of a terminal electron acceptor. Though the exac

practical basis for determining ΔGoCox has been validated (Arndt et al., 2013; LaRowe and Van Cappellen, 2011; Graham et al., 2017; Boye et al., 2017; Stegen et al., 2018).

3.4 Stream solute tracer

Two injections of a conservative solute tracer (NaCl) were conducted at 46 synoptic sites, one each at the upstream and downstream reach boundaries to quantify discharge and short-term hyporheic flux. First, we fixed the upstream end of the study reach at the same transect as the piezometer and sampling location. Next, we set the downstream station at a distance of about 20 wetted channel widths downstream from the piezometer and sampling location, a length selected to capture a representative valley segment (after Anderson et al., 2005). Minor variation in distance was allowed to place two specific conductivity sensors in well-mixed locations within the stream channel, with the total length reported for each tracer study reach. For each injection, mixing lengths for the solute tracer were visually estimated (after Payn et al., 2009; Ward et al., 2013b, 2013a), and small releases of a visual tracer were used to confirm mixing lengths when visual estimates were uncertain. A known mass of NaCl was dissolved in stream water and released as an instantaneous injection one mixing length upstream from the reach boundary. Initially, the downstream slug was released and measured only at the downstream location to enable dilution gauging estimates of discharge at the downstream end of the study reach. Next, the upstream slug was released and monitored at both locations to enable dilution gauging at the upstream transect, and evaluation of both recovered and lost tracer along the study reach. The experimental design closely follows Payn et al. (2009) and Ward et al. (2013b).

Solute tracer data at the reach boundaries were recorded as specific conductance (Onset Computer Corporation, Bourne, MA, USA). We used a four point calibration curve constructed by dissolving known masses of NaCl in stream water to convert specific conductance to salt concentration ($C = 0.5022S$; where C is NaCl concentration in mg/L and S is specific conductance; $r^2 > 0.99$). Notably, this equation does not include a y-intercept as we first subtracted background S from all observations prior to conversion. In addition to providing the full solute tracer timeseries in the data set, we also provide estimates of discharge (Q) based on dilution gauging, truncating the recovered tracer timeseries after 99% recovery (after Mason et al., 2012; Ward et al., 2013b, 2013a). We report in the data set Q for both the upstream and downstream ends of the study reach, and the change in Q along the study reach. Several additional metrics describing solute tracer timeseries are detailed in Ward et al. (2019).

4. Data Availability

These data are archived in the Consortium of Universities for the Advancement of Hydrologic Science, Inc. (CUAHSI) HydroShare data repository, accessible as http://www.hydroshare.org/resource/f4484e0703f743c696c2e1f209abb842 . In

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Identification of putative biochemical transformations using FT-ICR-MS¶
To identify potential biochemical transformations, we followed the procedure detailed by Breitling et al. (2006) and employed by Bailey et al. (2017), Graham et al. (2017), Graham et al. (2018), Moritz et al. (2017), Kaling et al. (2018), and Stegen et al. (2018). The mass difference between m/z peaks extracted from each spectrum with S/N>7 were compared to commonly observed mass differences associated with biochemical transformations. All possible pairwise mass differences were calculated within each extraction type for each sample, and differences (within 1ppm) were matched to a list of 92 common biochemical transformations (e.g., gain or loss of amino groups or sugars). For example, a mass difference of 99.07 corresponds to a gain or loss of the amino acid valine, while a difference of 179.06 corresponds to the gain or loss of a glucose molecule. Pairs of peaks with a mass difference within 1 ppm of our transformation list were considered to be related by the corresponding compound. ¶

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addition to tabular data, timeseries for solute tracer experiments and detailed results from the FT-ICR-MS analyses are archived. Raw sequence data for 16S DNA analyses are archived at the U.S. National Center for Biotechnology Information (NCBI) as a BioProject (Accession: PRJNA534507).

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5. Conclusions

We provide here a detailed characterization of physical, chemical, and biological parameters that are germane to the study of river corridor exchange and associated ecosystem functions and services. These data represent state-of-the-science characterization conducted at a heretofore unpresented resolution in space, and the only known data set that integrates across physical, chemical, and biological dimensions of the river corridor, including coverage across 5 stream orders. Taken together, these data will enable the testing of hypothesized processes and relationships in the river corridor across spatial scales, and will be useful in the generation of testable hypotheses about river corridor exchanges in future studies.

Author Contributions.

All co-authors participated in the field collection, laboratory analysis, and/or curation of the data set. ASW was primarily responsible for the writing of this manuscript and assembly of the archival database. ASW and JPZ conceived of the study design with input from all co-authors. All authors contributed to the writing of this manuscript.

Competing Interests.

The authors report no conflicts of interest.

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