AGU PUBLICATIONS

Water Resources Research

RESEARCH ARTICLE

10.1002/2016WR019303

Key Points:

- The hyporheic zone (HZ) is a source of DIC to the stream
- During base flow periods, neither stream water nor groundwater nor hillslope soil water are significant sources of DOC or DIC to the HZ
- Most hyporheic DIC exported to the stream is generated by microbial respiration of buried particulate organic matter

Correspondence to:
H. A. Corson-Rikert,
hacorrik@gmail.com

Citation:
Corson-Rikert, H. A., S. M. Wondzell, R. Haggerty, and M. V. Santelmann (2016), Carbon dynamics in the hyporheic zone of a headwater mountain stream in the Cascade Mountains, Oregon, *Water Resour. Res.*, *52*, 7556–7576, doi:10.1002/2016WR019303.

Received 6 JUN 2016
Accepted 11 SEP 2016
Accepted article online 16 SEP 2016
Published online 1 OCT 2016

Carbon dynamics in the hyporheic zone of a headwater mountain stream in the Cascade Mountains, Oregon

Hayley A. Corson-Rikert[1], Steven M. Wondzell[2], Roy Haggerty[1], and Mary V. Santelmann[1]

[1]College of Earth, Ocean, and Atmospheric Sciences, Oregon State University, Corvallis, Oregon, USA, [2]U.S. Forest Service, Pacific Northwest Research Station, Corvallis, Oregon, USA

Abstract We investigated carbon dynamics in the hyporheic zone of a steep, forested, headwater catchment western Oregon, USA. Water samples were collected monthly from the stream and a well network during base flow periods. We examined the potential for mixing of different source waters to explain concentrations of DOC and DIC. We did not find convincing evidence that either inputs of deep groundwater or lateral inputs of shallow soil water influenced carbon dynamics. Rather, carbon dynamics appeared to be controlled by local processes in the hyporheic zone and overlying riparian soils. DOC concentrations were low in stream water (0.04–0.09 m*M*), and decreased with nominal travel time through the hyporheic zone (0.02–0.04 m*M* lost over 100 h). Conversely, stream water DIC concentrations were much greater than DOC (0.35–0.7 m*M*) and increased with nominal travel time through the hyporheic zone (0.2–0.4 m*M* gained over 100 h). DOC in stream water could only account for 10% of the observed increase in DIC. In situ metabolic processing of buried particulate organic matter as well as advection of CO_2 from the vadose zone likely accounted for the remaining 90% of the increase in DIC. Overall, the hyporheic zone was a source of DIC to the stream. We suggest that, in mountain stream networks, hyporheic exchange facilitates the transformation of particulate organic carbon buried in floodplains and transports the DIC that is produced back to the stream where it can be evaded to the atmosphere.

1. Introduction

Aquatic ecosystems process carbon on timescales that are short in comparison to timescales of carbon production, cycling, and storage in terrestrial ecosystems [*Battin et al.*, 2008]. As a result, streams and rivers play an active role in global carbon cycling [*Cole and Caraco*, 2001; *Regnier et al.*, 2013]. Terrestrial carbon enters streams through direct inputs such as leaf-fall and throughfall, and through subsurface flow. Once in streams, terrestrial carbon is not only advected to downstream reaches, but is also transformed, evaded, and stored. Understanding the physical and biogeochemical controls on carbon transformation in aquatic ecosystems is critical because rates of carbon transformation influence the movement of carbon through a system and determine the form in which it is exported.

Headwater streams are particularly important locations for the transformation of terrestrially derived organic carbon because these streams make up 75% of global stream length [*Downing et al.*, 2012], receive large amounts of carbon from adjacent terrestrial ecosystems, and continuously exchange water with streambed sediments and adjacent floodplains [*Kasahara and Wondzell*, 2003; *Battin et al.*, 2008; *Wondzell*, 2011]. This exchange, defined as hyporheic exchange flow, increases the residence time of organic molecules that are transported by the stream water and simultaneously increases their exposure to biofilms and aggregates that dominate microbial communities in the subsurface. It also provides these communities with a steady supply of oxygen and nutrients [*Battin et al.*, 2008]. As a result, organic matter is actively processed and metabolized in hyporheic zones, and large quantities of CO_2 are generated via respiration [*Grimm and Fisher*, 1984; *Findlay et al.*, 1993; *Pusch and Schwoerbel*, 1994; *Pusch*, 1996; *Mulholland et al.*, 1997; *Baker et al.*, 1999; *Battin*, 1999; *Sobczak and Findlay*, 2002].

Several studies have examined the transformation of DOC along hyporheic flow paths through gravel bars located within active stream channels where hyporheic water does not mix with water from other sources. These studies showed that the hyporheic zone was a sink for DOC and a source of DIC, with consumption of DOC and O_2 and production of DIC occurring along a gradient of travel distances, or travel times, through the hyporheic zone. Stream-source DOC was a critical input to the hyporheic zone and accounted for 50%–85% of the heterotrophic respiration that occurred along hyporheic flow paths, with the remainder accounted for by POC buried in gravel bar sediment [*Findlay et al*., 1993; *Jones et al*., 1995; *Sobczak and Findlay*, 2002; *Zarnetske et al*., 2011]. However, the simplified setting of an unvegetated gravel bar and the dominance of stream-source water in hyporheic flow paths within this setting limits the transferability of these results to other stream reaches.

Patterns of change in concentrations of DOC along hyporheic flow paths through forested riparian zones in mountain streams likely differ from those in midchannel gravel bars. Particulate organic matter buried in the hyporheic sediment may be a source of DOC for both the hyporheic zone and the stream [*Schindler and Krabbenhoft*, 1998]. Also, lateral inputs of shallow soil water and vertical leaching from the overlying soil organic horizons could serve as sources of DOC and deeper, long-residence time ground water might serve as a source of DIC. These additional inputs of DOC or DIC would influence subsurface carbon cycling and could potentially distort or obscure simple patterns of carbon metabolism previously observed along hyporheic flow paths [*Sobczak and Findlay*, 2002; *Zarnetske et al*., 2011].

This study focuses on the seasonal dynamics of DOC and DIC within the floodplain of a small mountain stream during base flow periods. Our starting conceptual model builds on the work of *Findlay et al*. [1993], *Jones et al*. [1995], and *Zarnetske et al*. [2011], postulating that stream-source DOC will be the primary source of organic carbon for heterotrophic respiration in the hyporheic zone and that residence time will be the major factor determining the amount of DOC consumed and DIC produced along hyporheic flow paths. Previous research at this site lends substantial support for our conceptual model. First, ground water flow models calibrated to the site suggested that the median hyporheic residence time was 17 h, and that residence times along some hyporheic flow paths stretched to several weeks [*Kasahara and Wondzell*, 2003]. These simulation results also suggested that, at base flow, the turnover length of stream water through the hyporheic zone was less than 100 m and that lateral inputs of shallow soil water or deeper groundwater did not substantially influence hyporheic flow paths through the study site. These model results were well supported by tracer tests which were conducted across a range of discharges and suggested that the residence times and magnitudes of hyporheic exchange fluxes change little with changes in stream discharge over a wide range of base flow conditions [*Wondzell*, 2006; *Ward et al*., 2012; *Voltz et al*., 2013; *Ward et al*., 2016].

Nonetheless, because the chemistry of stream water at our study site is dilute, relatively small volumes of DOC or DIC-rich water from lateral inflow could have a significant influence on concentrations of dissolved carbon at different locations within the hyporheic zone. As a result, we also examine the degree to which different source waters might influence DOC and DIC dynamics in the hyporheic zone during base flow periods, and how this influence might change between the summer dry season and the fall and early-winter wet season.

The mixing of different source waters can be deciphered using end-member mixing analyses (EMMA). These analyses are used to discern the relative proportion of water contributed by each source, as well as how that proportion varies in response to changing catchment wetness. The EMMA approach is typically applied to whole catchments and has been used to examine how mixing controls changes in the quantity [McGlynn *and McDonnell*, 2003] and quality [*Inamdar et al*., 2011] of DOC. Here, we apply EMMA to examine the potential influence of mixing of different source waters on the concentrations of DOC and DIC observed during base flow periods within a well network located in the floodplain of a mountainous, headwater stream.

The focus of our study was to investigate carbon dynamics in the hyporheic zone of a headwater catchment in the Western Cascade Mountains of Oregon. We compare the influence of hyporheic biogeochemical processes to the influence of mixing of different source waters, and examine how the relative importance of these processes changed from the summer dry season to the winter wet season.

2. Study Site

This study was conducted in the lower portion of Watershed 1 (WS1), a study watershed in the H.J. Andrews Experimental Forest, located in the Western Cascades of Oregon, USA (44° 12′ 28.0′N, 122° 15′ 30.0′W; Figure 1). WS1 is a steep, forested catchment that is 95.5 ha in size, and ranges in elevation from 450 to

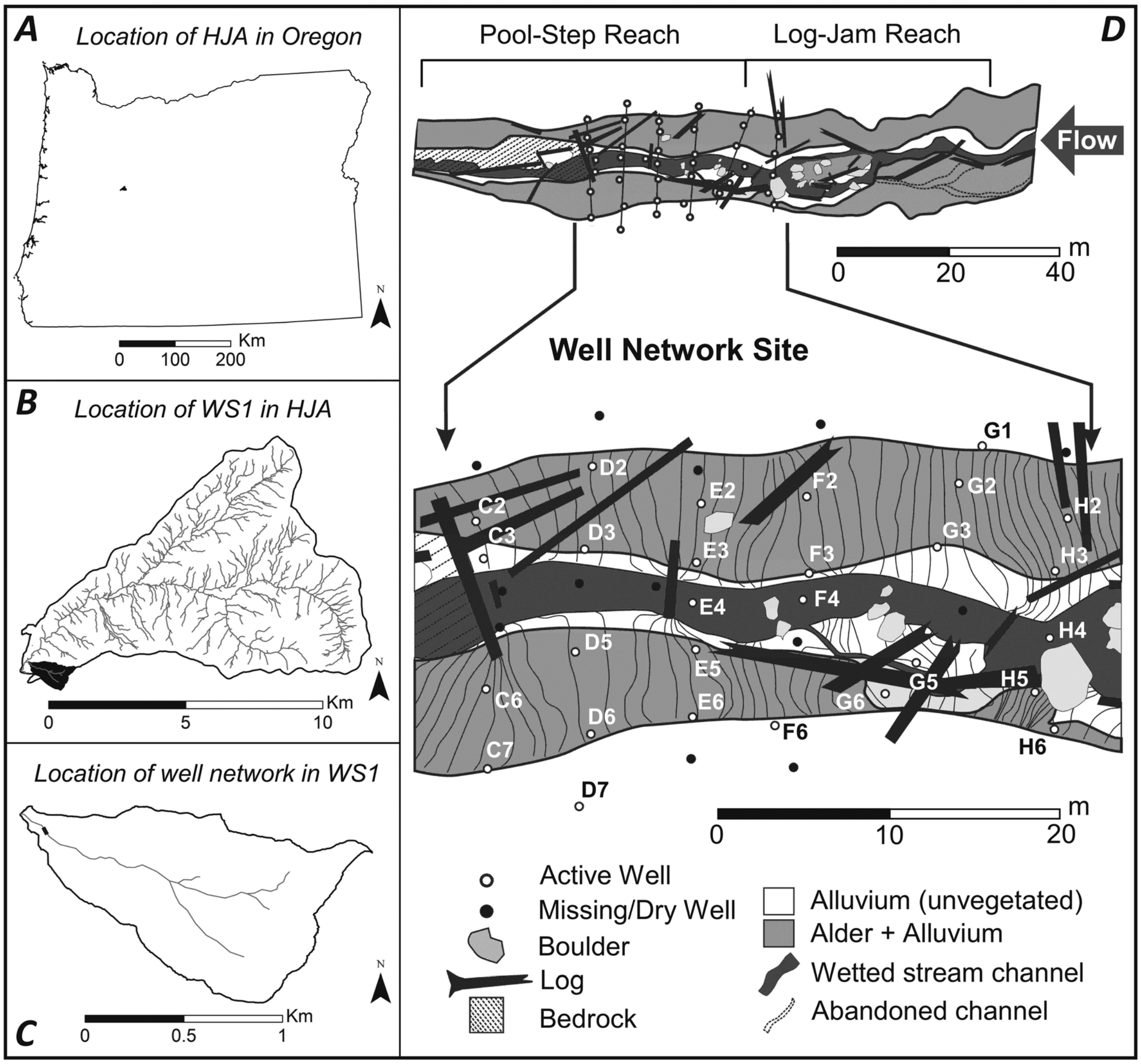

Figure 1. (a) Location of the H.J. Andrews Experimental Forest within Oregon, and (b, c) location of Watershed 1 and the well network within H.J. Andrews. Note that flow is from right to left in the well network figure. All wells that were sampled are active wells and are labeled. Data sources: (d) the image of the well network site was modified from *Wondzell* [2006]; the catchment outlines and stream networks are from the H.J. Andrews Experimental Forest; the Oregon outline is from ESRI and TomTom.

1027 m. The climate is characterized by cool, wet winters, and warm, dry summers. At lower elevations, air temperatures range from an average of 1°C in January to 18°C in July. The 2300 mm of annual precipitation falls primarily as rain from November to March. WS1 lies within the transient snow zone, where snow accumulates during cold winter storms, but melts during warm periods or warmer storms, so that snow packs do not persist for the entire winter. As a result, peak streamflow in WS1 occurs anytime throughout the winter and declines in summer months. Streamflow becomes so low in July, August, and September that surface flow cannot be continuously sustained, and the stream becomes spatially intermittent.

From 1962 to 1966, WS1 was 100% clear-cut using skyline yarding to lift logs clear of the ground and thereby minimize soil disturbance as logs were removed from the watershed. In 1966, the logging debris (slash) was burned [*Levno and Rothacher*, 1969; *Halpern and Franklin*, 1990]; many burned logs and debris were left in the riparian zone. Today, dense stands of Douglas fir and hemlock dominate on hillslopes. Red alder dominates the riparian zone, although maple and cottonwood are also present [*Rothacher et al.*, 1967; *Halpern and Franklin*, 1990; *Johnson and Jones*, 2000]. The alders became established after the logging operation, and today are being overtopped by Douglas fir. As a result, many have died or fallen in recent years.

Table 1. Sampling Information and Hydrologic and Climatic Conditions for Each of Seven Base Flow Sampling Runs[a]

Run	Date	No. Wells Sampled	Avg. Air T (°C)	Avg. EC (μS/cm)	Avg. Stream T (°C)	Avg. Q (L/s)	5 Day ppt Total (mm)	21 Day ppt Total (mm)
B	25 Jul 2013	16	29.9	52.7	15.6	1.3	0.0	0.0
C	22 Aug 2013	25	27.1	56.7	15.5	0.5	0.0	10.9
D	19 Sep 2013	28	20.9	53.5	12.8	1.0	4.1	37.9
E	28 Oct 2013	28	7.6	45.2	8.7	4.1	8.9	20.0
F	15 Nov 2013	28	5.3	42.9	8.0	7.7	2.9	94.3
G	8 Dec 2013	28	−6.0	34.6	1.5	18.0	11.2	149.1
H	16 Mar 2014	28	13.1	35.4	8.3	34.2	0.4	291.9

[a] Climatic data and hydrologic data courtesy of the PRIMET meteorological station and WS1 gaging station at the H.J. Andrews Experimental Forest, Oregon.

The stream channel in WS1 is steep and is usually confined. It has been shaped by debris flows, which have scoured the stream to bedrock in places. Reaches where colluvium is deposited are less constrained. Our study site is located in a zone of colluvial deposition near the base of WS1. The channel remains steep, with an average longitudinal gradient of 14%. The poorly sorted colluvial sediment is up to 2 m thick across the 14 m wide valley floor and the channel is broken into a series of pools and steps that have formed over logs and boulders [*Wondzell*, 2006]. These steps drive 50% of hyporheic exchange between the stream and subsurface [*Kasahara and Wondzell*, 2003]. During high and low base flow, downvalley hydraulic gradients along this reach are, on average, 1.4 times steeper than cross-valley gradients, leading to the development of extended flow paths parallel to the stream and to the predominance of long-timescale hyporheic exchange [*Wondzell*, 2006; *Voltz et al.*, 2013], with median residence times estimated at 17 h [*Kasahara and Wondzell*, 2003]. Despite these long residence times and abundant organic carbon, hyporheic water in WS1 was generally oxic (Serchan, unpublished data, 2014).

The well network was installed in 1997 [*Wondzell*, 2006] and originally consisted of 30 shallow (~1–1.7 m deep) riparian wells and 7 in-stream piezometers arrayed in six transects that span the width of the valley, perpendicular to the direction of streamflow (Figure 1). We were able to sample 24 wells and 4 piezometers—9 of the original were cracked, missing, or had gone dry. Both wells and piezometers are constructed of 3.175 cm (1 1/4 inch) schedule 40 PVC. An array of drilled holes serves as a screen along the bottom 50 cm of the wells and bottom 5 cm of the in-stream piezometers. The deepest well extends to 1.7 m, but the majority are approximately 1 m deep. We also sampled one hillslope well, located approximately 150 m up the watershed at the base of a hillslope hollow, which we installed during the summer of 2013.

3. Methods

3.1. Preparatory Methods

We prepared all equipment and filters for fieldwork at the Institute for Water and Watersheds (IWW) Collaboratory at Oregon State University using operating procedures developed by the Oregon State University and United States Forest Service Cooperative Chemical Analytical Laboratory (CCAL). This equipment included 40 mL borosilicate vials, 250 mL Nalgene HDPE bottles, VWR 60 mL syringes with BD Luer-Lok tips, Cole-Parmer polycarbonate stopcocks with Luer connections, 4.7 cm Whatman grade GF/F glass microfiber filters, a 4.7 cm filter apparatus, and 0.635 cm (1/4 inch) sample tubing. All syringes, bottles, vials, tubing, and stopcocks were acid washed in 10% v/v HCl acid bath, and vials for DOC analysis were also baked in a muffle furnace at 550°C for 3 h. The GF/F filters were rinsed, dried, and baked in a muffle furnace at 500°C for 3 h [*CCAL*, 2013]. Note that the use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

3.2. Field Methods

On the afternoon prior to each sampling run, we recorded the pH and temperature of each well and the stream using a YSI 60 probe, and determined the depth to water in each well relative to ground surface. Following this, we removed and discarded 700 mL from each well using a designated purge syringe and tubing.

The following morning (on the date given for each sampling run in Table 1), we sampled each of the 28 wells, the stream, and the hillslope well, collecting one field duplicate for every ten samples. We extracted

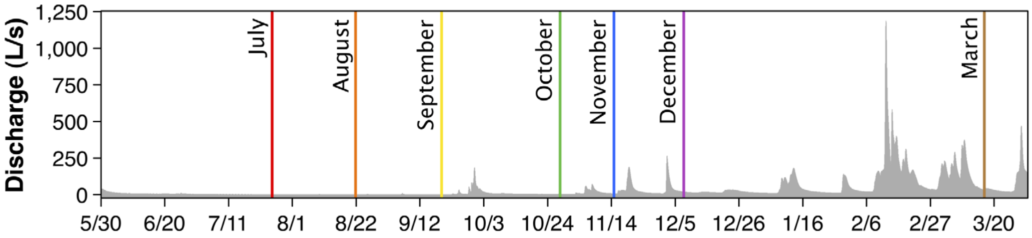

Figure 2. Timing of monthly sample collections (vertical lines) during 2013 and 2014. The stream discharge over this period is shown in gray shading. Discharge data are from the WS1 gaging station at H.J. Andrews Experimental Forest, Oregon.

water from the wells using the acid washed 60 mL syringes, stopcocks, and 0.635 cm sample tubing. Prior to sample collection, we rinsed the sample tubing and syringes, GFF filters, and 250 mL bottles with the sample water. We then collected 250 mL of water for DOC, anion, cation, and alkalinity analysis, which we filtered in the field through the prepared GFF filters. We collected sample aliquots for DIC analysis last so as to minimize exposure of the water to the atmosphere, and preserved each sample in an individual, locked, airtight syringe. We sampled stream water using this same technique. On two occasions, 250 mL of unfiltered stream and well water were collected for TOC analysis. We transported all samples back to the lab on ice and kept them in cold storage until analysis.

We sampled the WS1 well network at monthly intervals from July to December 2013 and then again in March 2014, focusing our sampling during base flow or near-base flow periods after relatively dry antecedent conditions (Figure 2 and Table 1). We obtained discharge, stream temperature, and stream chemistry data from the WS1 gaging station, located approximately 50 m below the well network. We obtained air temperature and both precipitation amount and chemistry data from the PRIMET meteorological station at the H.J. Andrews headquarters, located approximately 0.6 km from our study site.

3.3. Laboratory Methods

We conducted all analytical work in the IWW Collaboratory at Oregon State University. We measured concentrations of DOC and DIC on a Shimadzu TOC-VSCH Combustion Carbon Analyzer. We determined concentrations of major anions on a Dionex 1500 Ion Chromatograph and concentrations of major cations on a Perkin-Elmer AAnalyst-100 Atomic Absorption Spectrometer. We measured total alkalinity by titrating all samples to a pH of 4.5 on a Radiometer TIM840 AutoTitrator. We performed all analyses according to standard operating procedures that were developed primarily from APHA methods by the Oregon State University and United States Forest Service Cooperative Chemical Analytical Laboratory. Detailed methods and method detection limits are described in *Corson-Rikert* [2014].

3.4. Graphical Analysis

Spatial patterns in chemical and physical parameters within the well network were interpolated and displayed as a contoured z-value on an *x-y* surveyed grid by using Delaunay triangulation to create a triangulated irregular network.

3.5. Travel Time Analyses

Nominal travel times—the time required for water to flow from the stream to each well—were not measured during the sampling period in this study. Also, we could not use travel times calculated from a 1997 stream-tracer injection [*Wondzell*, 2006] because the morphology of the channel has changed over time, leading to changes in hyporheic travel times for some wells. A series of tracer tests were conducted in 2010 [*Ward et al.*, 2016] and a multiday tracer test was conducted in 2015 (Pennington, unpublished data). Neither are ideal for our purposes. First, tracer arrival break-through curves were not measured in all the wells during each tracer test. Also, the 2010 tracer tests occurred 4 years before our study; the 2015 tracer test occurred after the original PVC wells with 50 cm screens were replaced at the same locations with 5 cm diameter, stainless steel well casings with 10 cm screens. The differences in well design, and continuing changes to the channel morphology, could lead to some error in our estimate of travel times through the hyporheic zone during our study. In order to assemble the most complete data set of travel times, we combined results from the two studies, averaging the measured travel times where data for a given well were available from both tracer tests.

We adjusted the median travel time measured at each well for the in-channel advection time. Our wells are arranged in transects perpendicular to the channel (Figure 1), and tracer break-through curves were collected at the midchannel piezometers. Thus, we calculated the nominal travel time by subtracting the median in-stream travel time to a given well transect from the median travel time for each well along that transect. Note that, at summer low flow, in-channel travel times through our study reach exceed 2 h and could substantially overestimate the hyporheic travel time for wells located close to the stream where travel times may be as short as 1 h. However, this correction for in-channel advection will have little influence on wells located far from the stream where hyporheic travel times are typically 1 to several days.

3.6. Comparison of Lateral Groundwater Inputs Versus Down Valley Subsurface Fluxes

We compared the relative magnitude of lateral groundwater inputs to downvalley subsurface flows in order to estimate the potential for lateral inputs to influence spatial patterns of water chemistry observed in our well network. To do this, we estimated downvalley hyporheic flows using Darcy's law and estimated potential lateral inputs based on the proportion of the total watershed area that drains directly into the well network.

Previous work as well as head measurements made from the well network clearly show that, at periods of base flow discharge, subsurface flow paths through the valley floor are oriented down valley and parallel to the stream [*Kasahara and Wondzell*, 2003; *Wondzell*, 2006]. Under these conditions, it is relatively straightforward to measure both head gradients and the saturated cross-sectional area perpendicular to the subsurface flow paths and to use these to calculate subsurface flows. We measured water table elevations prior to sampling each well so that head gradients ($\Delta h/\Delta L$) could be calculated directly from our measurements. The wells had been driven to refusal depth, which is presumed to be the underlying bedrock surface. Exposures of bedrock in the stream channel are consistent with this interpretation. Thus, the saturated thickness of the aquifer can be calculated from the measured height of water in the wells and the total depth of the well. The valley width along each well transect and the location of each well are known from cross-sectional surveys. Thus, the cross-sectional saturated area, perpendicular to the downvalley flow could be calculated ($A=w*d$). Finally, saturated hydraulic conductivities (K) were available from previous slug tests [*Kasahara and Wondzell*, 2003] and were validated with well-to-well tracer experiments [*Kasahara*, 2000]. The width of the valley floor was divided into segments, with one well located in the center of each segment, and the subsurface flux was calculated independently for each segment and summed to give the total downvalley subsurface flow ($Q_{\text{downvalley}}$) for each sample date.

We calculated the potential direct hillslope drainage into our study reach from a detailed LIDAR-based DEM covering the entire watershed. We first extracted the stream centerline and smoothed it using a 15 m moving average to identify the dominant flow direction of the valley floor. Valley floor segments, approximately 1 m in length, were defined by where lines perpendicular to the smoothed valley centerline intersected the hillslope (2 m above the smoothed valley centerline after *Jencso et al*. [2009]). We calculated the upslope accumulated area (*UAA*) draining into each valley floor segment using a multiple flow-direction algorithm [*Seibert and McGlynn*, 2007] implemented with TopoToolbox in MATLAB [*Schwanghart and Kuhn*, 2010]. We then extracted just those valley segments and associated *UAA*s in which our well network was located, and summed the *UAA* to determine the total hillslope area draining directly into the well network reach ($\sum UAA_{\text{study-reach}}$). We assumed that hillslope contribution to base flow discharge was a simple linear function of watershed area, and estimated lateral inflows ($Q_{\text{lat-in}}$) by multiplying whole watershed stream discharge (Q) by the proportion of the watershed area draining directly to our study reach ($\sum UAA_{\text{study-reach}}$/Watershed Area). We used discharge recorded at the mouth of the watershed to estimate the potential $Q_{\text{lat-in}}$ for each sample date.

3.7. End-Member Mixing Analysis

We followed the methods described by *Christophersen and Hooper* [1992] and *Hooper* [2003] to examine the potential for mixing of different source waters to influence carbon chemistry in the hyporheic zone of our study site. We chose to use principle component analysis (PCA) because concentrations of different solutes are correlated, as are changes in those concentrations through time. By using PCA, we were able to use several solutes to define end-members, making for a much more robust analysis. Water chemistry has been monitored in this watershed since 2003, using 3 week, flow-proportional composited samples [see *Johnson and Fredriksen*, 2015 for more details]. We used data from the entire available period of record, from June 2003 through June 2014, and based our analysis on solutes that mix conservatively and were measured in three data sets: the stream, the precipitation at a nearby rain gauge, and the samples from our well network. The final solutes used in the analysis were Ca^{+2}, Mg^{+2}, Na^{+}, and Cl^{-}. The EMMA was based on a PCA of stream solute concentrations over the period of record. Concentration data were first standardized to mean = 0 and SD = 1 and the PCA used the resulting solute correlation matrix (# samples by # solutes). The first and second eigenvectors, together, explained 91% of the variation in the stream-water concentration of the four solutes used in the analysis. Thus our EMMA is based on a 2-D representation of the four-solute mixing space, known as the "U-space." We standardized our well network samples and rain chemistry samples by the means and standard deviations from the stream water data set and projected these into the U-space described by the first two eigenvectors from the PCA.

We conducted simple linear regression between either DOC or DIC and the two PCA axes to help interpret the results of the EMMA and to explore the likelihood that mixing of different source waters explained the observed variation in carbon chemistry within the well network on any given sample date. We contrasted end-member mixing with internal biogeochemical reactions as potential explanations for the observed chemistry by also conducting simple linear regressions between either DOC or DIC and nominal travel time (total travel time minus the in-stream travel time), distance from the stream channel, and the depth of the overlying unsaturated soil. All analyses were conducted in SAS, the Statistical Analysis Software, v 9.4.

4. Results

4.1. Seasonal Patterns in DOC, DIC, Cl^{-}, and Ca^{+2}

DOC and DIC concentrations within the well network showed distinct seasonal trends (Figures 3a and 3b). We observed greater variation in DOC concentrations and higher peak DOC concentrations during fall and winter months, particularly October and November (Figure 3a). DIC concentrations were greatest in summer months, declined during the fall, and reached a minimum in December (Figure 3b).

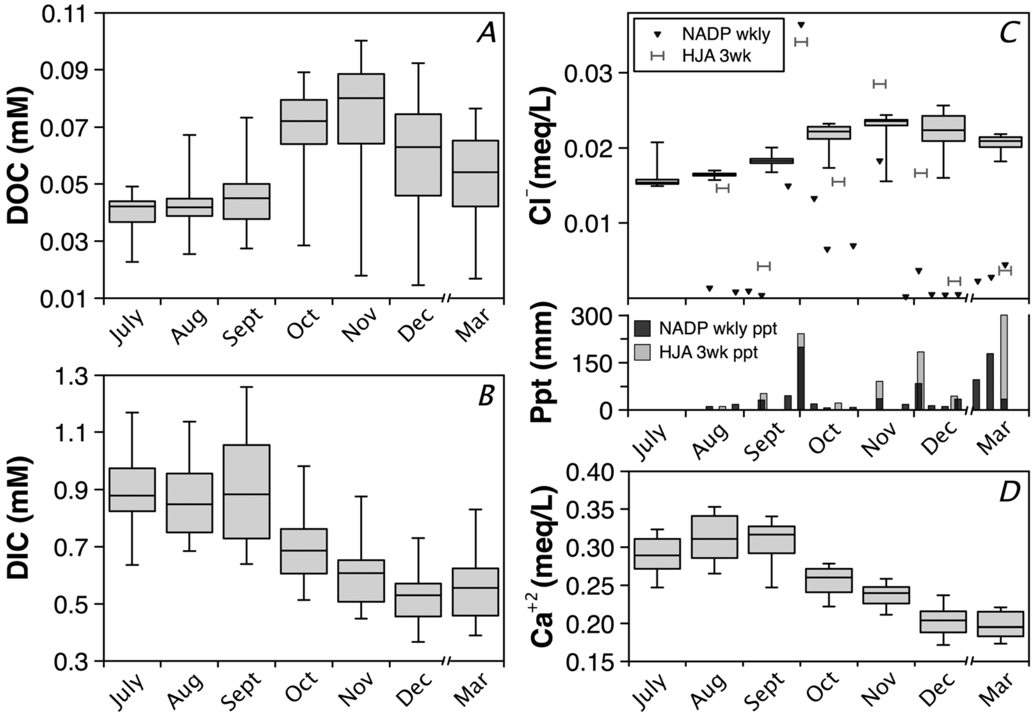

Figure 3. (a) Boxplots of DOC, (b) DIC, (c) Cl^{-}, and (d) Ca^{+2} concentrations in all sampled wells. Whiskers extend to extreme data points and indicate the range. Chloride concentrations in precipitation, and precipitation amounts are also shown in Figure 3c. Precipitation chemistry is from weekly National Atmospheric Deposition Program (NADP) samples and from 3 week bulked samples collected at the PRIMET meteorological station at H.J. Andrews Experimental Forest. Symbols were located using the end date for each weekly (NADP) or 3 week (HJA) sampling period.

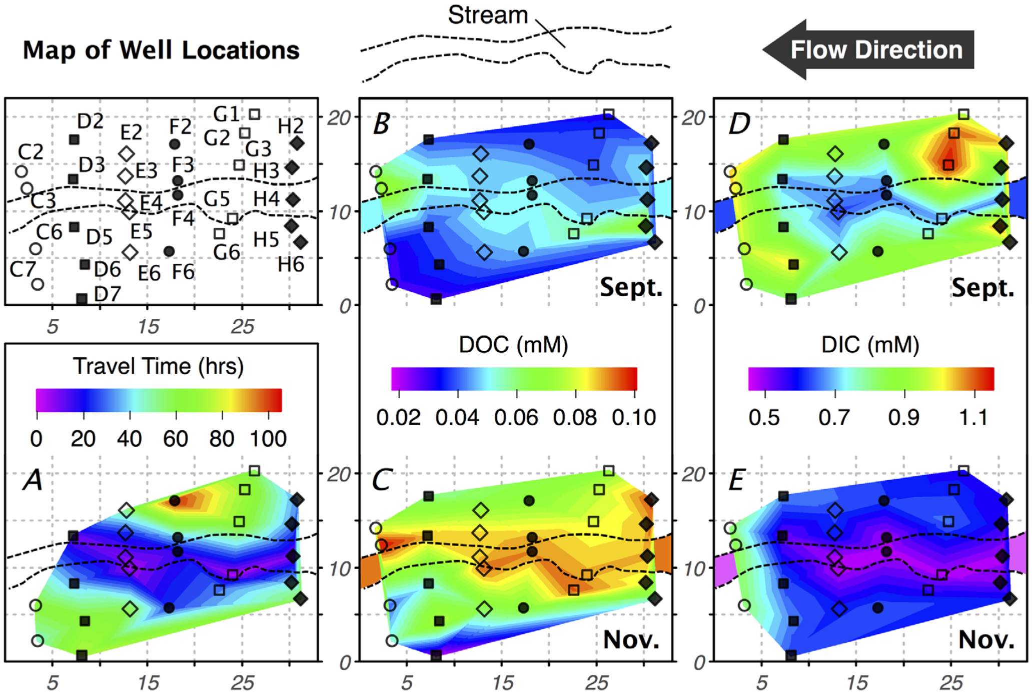

Figure 4. (a) Spatial patterns in the nominal travel time, DOC concentrations within the well network in (b) September and (c) November, and DIC concentrations within the well network in (d) September and (e) November. All data for the subsurface are represented in the contoured grid. Stream values are shown within the stream outline at the edges of the grid. Well locations are given in the top left plot, and match the orientation of Figure 1. The stream flows from right to left.

We observed a seasonal shift in chloride concentrations within hyporheic water (Figure 3c). Chloride concentrations were low in summer, increased with the onset of wet weather through the fall and early winter, and then decreased slightly by March. Chloride concentrations observed in either the stream water or well water samples were almost always higher than those observed in precipitation. Seasonal changes were also observed for Ca^{+2} concentrations, but these were opposite those observed for Cl^{-}. Concentrations of Ca^{+2} in hyporheic water were highest during the summer, declined throughout the fall, and were lowest in winter and spring (Figure 3d). Seasonal patterns in the concentrations of Mg^{+2}, Na^{+}, K^{+}, and total alkalinity were similar to those shown for Ca^{+2}.

4.2. Spatial Variability in Chemical and Physical Variables

Concentrations of DOC and DIC showed strong spatial patterns through the hyporheic zone, and while the absolute concentrations changed seasonally, the spatial patterns were relatively persistent. We illustrate this seasonality for two sample periods (Figure 4): September, representing the dry summer and early autumn period, and November, representing the wet autumn and early winter months. DOC concentrations in both September and November were highest within, beneath, and alongside the stream corridor, although pockets of elevated DOC were visible within the riparian zone, particularly in November (Figures 4b and 4c). DOC concentrations were lowest along the base of the adjacent hillslopes. Seasonal differences and within-month spatial patterns showed similar, but inverted trends for DIC. Concentrations of DIC were lower in November than in September, and DIC concentrations were lowest alongside and beneath the stream as well as within the stream water (Figures 4d and 4e). Hotspots of high DIC concentrations were visible in both months (e.g., well G3 in September).

4.3. EMMA Results

The end-member mixing analysis showed that the first and second eigenvectors, together, explained 91% of the variation in the stream-water concentration of the four solutes used in the analysis. The base cations, Ca^{+2}, Na^{+}, and Mg^{+2} all had positive loadings on the first eigenvector and loadings near the origin on the second eigenvector; Cl^{-} was opposite, with positive loading on the second eigenvector and loadings near the origin on the first eigenvector (Figure 5a).

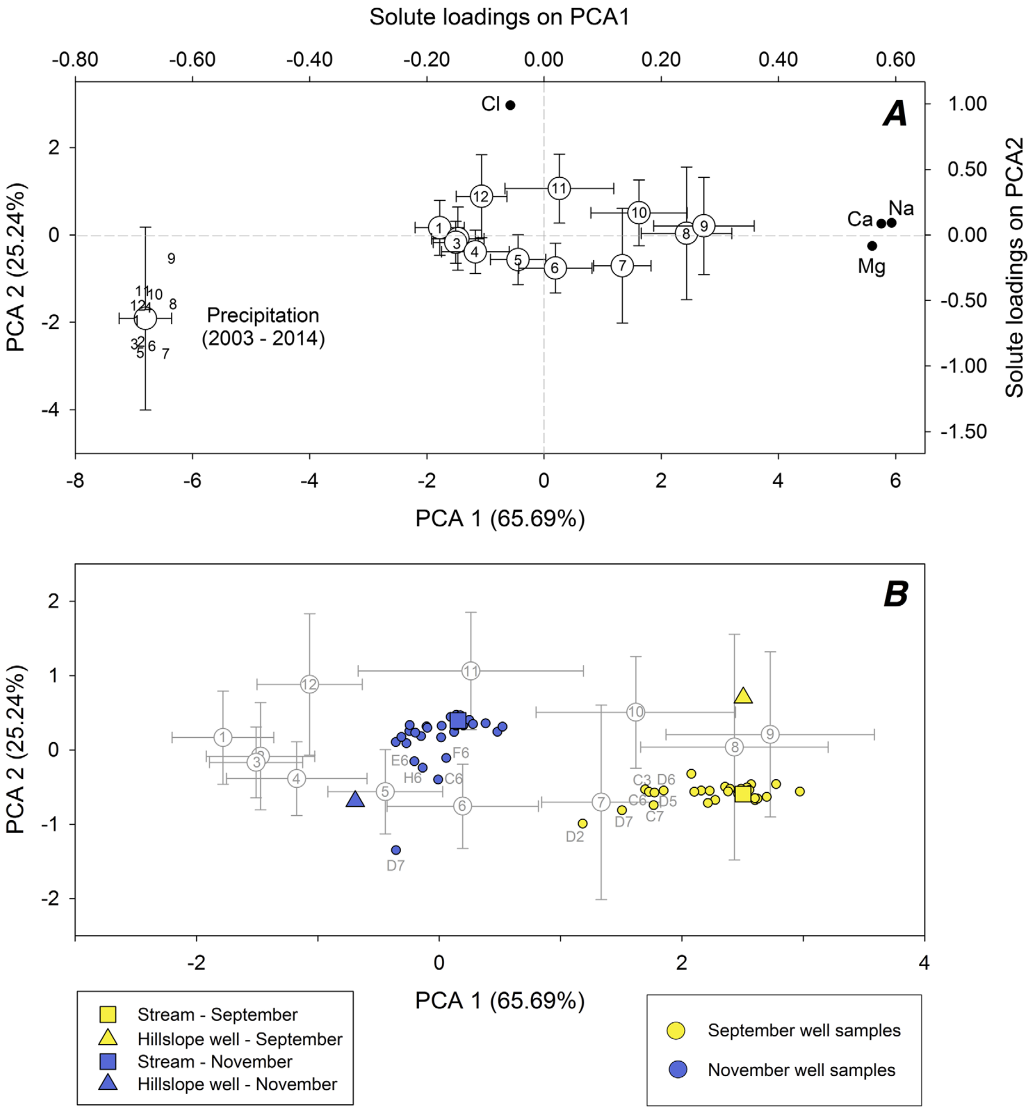

Figure 5. (a) Scores for water samples collected between 2003 and 2014 in 3 week composited samples at the outlet of WS1 plotted in the U-space determined from EMMA of long-term stream water chemistry and based on Ca^{+2}, Na^{+}, Mg^{+2}, and Cl^{-}. Filled black dots show loadings of each solute on the first and second-PCA axes. Large, open, numbered circles represent stream water samples for each month of the year (January = 1; December = 12). Horizontal and vertical bars represent 1 standard deviation. Only the annual mean and annual standard deviations are shown for precipitation, with numbers representing the mean location for samples in each month of the year; (b) Scores for water samples collected from the well network, stream, and hillslope well plotted over the U-space defined in Figure 5a. We only plot data from two monthly sample dates: September to illustrate the patterns observed during late-summer low flow and November to illustrate patterns observed during high-base flow in the late autumn. Well samples plotting at a distance from the stream water are labeled.

The monthly mean scores of stream water plot in a counterclockwise loop as a result of changes in the concentrations of the solutes over the course of the year (Figure 5a). Stream water plots closest to precipitation chemistry from January through April. By May, stream water chemistry begins to shift to the right, a trend that continues through the summer. By September, when the stream reaches its annual minimum discharge and concentrations of base cations reach their annual maximum, stream water plots furthest to the right. As the watershed wets up with the onset of the rainy season in October, stream water chemistry shifts back to the left. During this period, stream water scores become more positive on the second eigenvector, indicating an increase in Cl^{-} concentrations in stream water, whereas during the summer stream water scores become more negative on the second eigenvector, reflecting lower Cl^{-} concentrations (Figure 5a).

Precipitation samples, averaged over the same time period, were always more dilute than stream water with respect to the four solutes used in the EMMA and thus plot in the lower left of the diagram (Figure 5a).

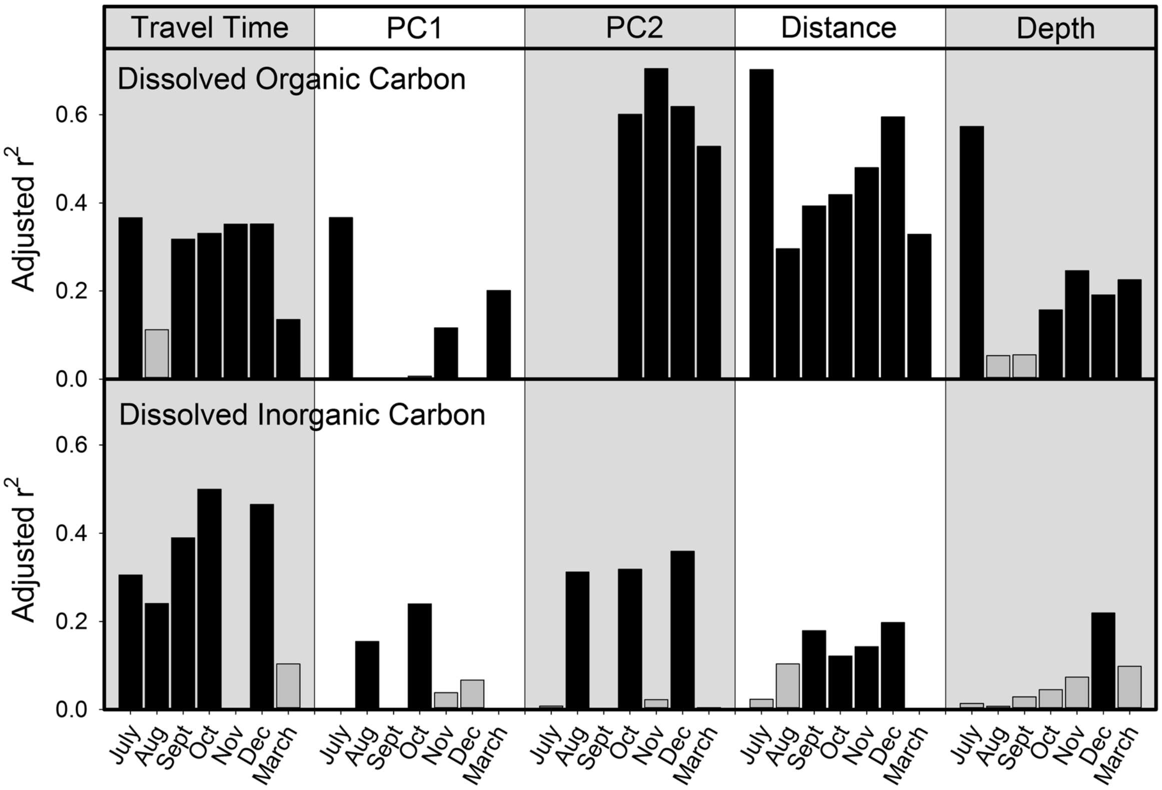

Figure 6. Simple linear regression results between either DOC or DIC (dependent variable) and a single independent variable. Independent variables regressed against the dependent variables were nominal travel time (total travel time minus the in-stream travel time), PCA1, PCA2, distance from the stream channel, and the depth of the overlying unsaturated soil. Bars indicate the strength of the correlation between the variables; black bars indicate regression slopes significantly different than zero ($p < 0.05$); gray bars are not significant. Note that all models included an intercept, but statistics on the intersect parameter are not presented here. Also note that, where r^2 is close to zero, the vertical bars are not visible; there are no missing data.

The monthly scores for precipitation show counterclockwise hysteresis, with largest variation along the second eigenvector. Monthly precipitation scores are lowest in late winter through midsummer, peak in late summer or early fall, and then decrease through late fall and winter. With the exception of September, the monthly mean scores for precipitation on the second eigenvector are always lower than those of stream water (Figure 5a). We do not have representative samples of other potential end members, such as soil water or deep groundwater.

Water samples collected from the stream and well network were plotted in the U-space determined from the PCA of long-term stream chemistry. We only show data from September, representing the dry summer and early autumn period, and November, representing the wet autumn and early winter months. The well water samples plot reasonably close to the long-term monthly means for stream water chemistry (Figure 5b), and the 2014 stream water grab samples plot within a single standard deviation of the respective monthly means. In September, water samples collected from wells show substantial variation along the first eigenvector, but little variation along the second eigenvector, with the exception of the hillslope well. Samples collected in November show less variation overall, although a few samples from riparian wells C6, E6, F6, H6, and D7, and from the hillslope well plot below the stream on the second eigenvector (Figure 5b).

Simple linear regression was used to examine whether mixing of different source waters (eigenvectors 1 and 2 from the PCA) or nominal travel time through the hyporheic zone best explained spatial patterns observed in the concentrations of DOC and DIC within the well network. Spatial changes in DOC were significantly correlated to the nominal travel times (Figure 6), though with relatively low r^2 values (0.11–0.37). Changes in DOC were slightly better correlated with distance from the stream, with DOC decreasing as both travel time (Figure 7a) and distance increased, except during the August sample period, which had the lowest regression slope. In comparison, DOC patterns observed within the well network were not consistently correlated to the first eigenvector (Figure 6). The r^2 was low in all months, except July, and regression

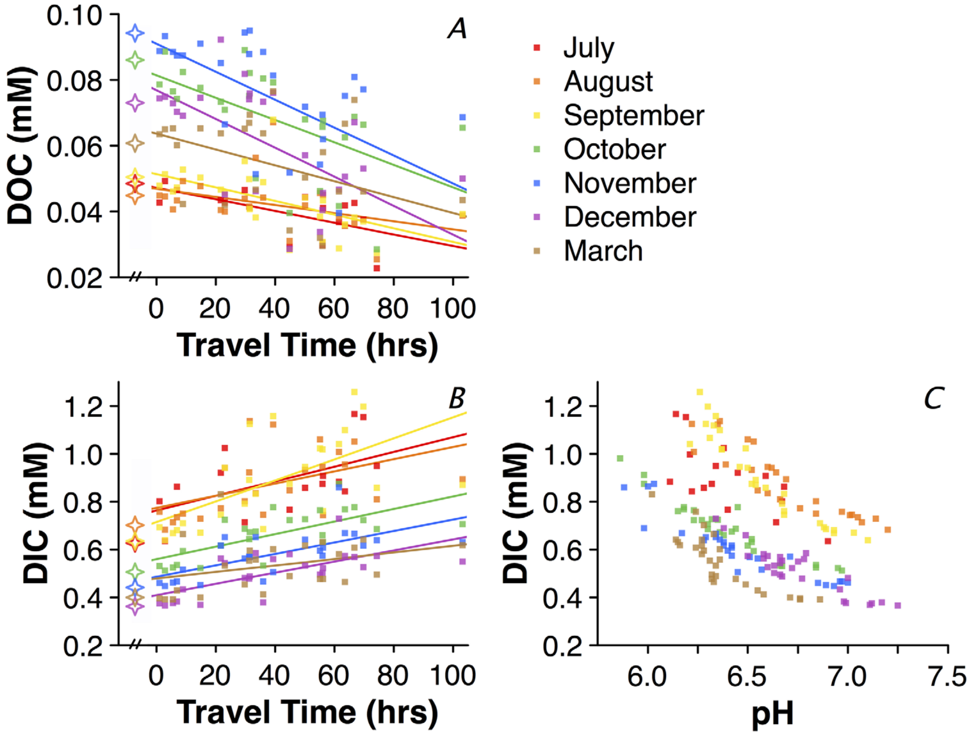

Figure 7. Relationships between key variables over the full study period. All of the included observations are from hyporheic wells. The stars in plots a and b indicate stream concentrations.

slopes were significantly different than zero in only three of seven sampling periods. The concentration of DOC was strongly correlated with the second eigenvector, but only during the wet season sampling periods, from October through March (Figure 6). Most water samples from the well network varied little along the second eigenvector as illustrated for the November sample period (Figure 5b), so that the regression of DOC against PC2 tended to be strongly leveraged by a small number of points. Spatial changes in DIC within the well network on each sampling date were more strongly correlated with nominal travel time than with any other independent variable in most monthly sample periods (Figure 6).

4.4. DOC and DIC Versus Nominal Travel Time

On each sample date, the concentration of DOC decreased and the concentration of DIC increased with travel time to each well (Figures 7a and 7b); all regression slopes were significantly different than zero ($p < 0.05$), except for DOC in August ($p = 0.057$) and DIC in both November ($p = 0.765$) and March ($p = 0.060$). The regression fits were weak. Nominal travel time only explained an average of 31% of the variation in DOC on sample dates when the regression slope was significantly different than zero; nominal travel time explained 38% of the variation in DIC. Within each monthly sample date, well water concentrations of DOC were usually lower than those observed in the stream (Figure 7a). For wells with nominal travel times greater than 40 h, concentrations of DOC were always lower than in stream water (Figure 7a). The DIC concentrations showed the opposite pattern, with DIC concentrations observed in the well water almost always higher than those observed in the stream water (Figure 7b). The variations in DIC observed on each sample date, and among sample dates, were strongly correlated to pH (Figure 7c).

5. Discussion

5.1. Mixing of Different Source Waters

Determining the cause of the observed changes in DOC and DIC along hyporheic flow paths is critical to understanding the role of the hyporheic zone in the watershed carbon budget. If the observed changes result from mixing of hillslope soil water or deeper groundwater with stream water across the width of the hyporheic zone, the hyporheic zone may have little influence on the watershed carbon budget.

Alternatively, if the observed changes result from biogeochemical transformations, then the hyporheic zone may exert critical control over carbon processing within the watershed.

Our results clearly show that spatial patterns of DOC and DIC observed in the well network are strongly correlated to both travel time along hyporheic flow paths and distance from stream. However, travel time and distance from the stream are themselves correlated because wells located at the base of the hillslopes along both valley margins all have long travel times. The products of biogeochemical transformations (e.g., the conversion of DOC to DIC) may accumulate along hyporheic flow paths, resulting in the observed patterns. Alternatively, lateral inputs of shallow soil water from the hillslopes could be influencing hyporheic chemistry along the valley margin. This influence would be expected to decrease across the floodplain as hillslope water mixes with stream-source water. However, this mechanism only has potential to account for the observed spatial patterns if lateral inputs are present and are characterized by low concentrations of DOC and high concentrations of DIC. Here, we use three lines of reasoning to examine the likelihood that different source waters mix within the well network: first, we compare the size of lateral inputs with the flux of water through the hyporheic zone; second, we examine water levels observed in the well network and the shape of the water table for evidence of lateral inputs; third, we review the results from the end-member mixing analysis (EMMA) for evidence that mixing of different source waters influences concentrations of either DOC or DIC.

5.1.1. Hillslope Accumulated Area and Lateral Inputs

Flow accumulation analyses based on the 1 m LIDAR-based DEM show that the hillslope area draining directly into the portion of the floodplain where the well network is located is quite small, accounting for only 0.8% of the total watershed area. If base flow stream generation is a simple function of contributing area, then these adjacent hillslopes would be expected to contribute 0.8% of the total streamflow to the channel through lateral inputs of shallow soil water, which would need to pass through the floodplain in which our well network is located. Much previous work has documented that subsurface flow paths through the steeply sloped valley are dominantly down valley and do not change substantially with variations in discharge [*Wondzell*, 2006; *Ward et al*., 2012; *Voltz et al*., 2013]. Thus, the down valley, subsurface flux of water through the floodplain, estimated from Darcy's Law, can be compared to lateral inputs expected from the upslope contributing area in order to determine the potential for lateral inputs to influence water chemistry within the floodplain.

Estimated down valley subsurface fluxes of water through the floodplain during base flow were 0.1 l/s, and did not differ between September and November. Late summer stream discharge during our September sample was 0.9 l/s so lateral inputs of shallow soil water (0.8% of WS1 area) might account for 0.007 l/s ($Q_{\text{lat-in}} = 0.008 \times 0.9$ l/s), which would constitute only 7% of the total down valley subsurface flow. Base flow stream discharge in November was 7.7 l/s, so estimated lateral inputs of soil water could be as much as 0.06 l/s ($Q_{\text{lat-in}} = 0.008 \times 7.7$ l/s), or 64% of the total down valley subsurface flow.

This simple flow budget analysis suggests that in late summer, lateral inputs of shallow soil water will be small so that subsurface flows through the valley floor will be dominated by stream source water. The situation is quite different in the wet season. After the watershed has wetted up from the fall rains, base flow discharge is much higher, presumably supported by much higher lateral inputs of groundwater or shallow hillslope soil water. If hillslope drainage area is a good predictor of the magnitude of these inputs at any point in the drainage network, then lateral inputs to our well network would be large relative to the total down valley flow and could have substantial influence on the observed water chemistry.

However, recent work by *Jencso et al*. [2009] has shown that lateral inputs from hillslopes to streams are not a simple linear function of upslope accumulated area (UAA). Rather, there is a curvilinear function that relates catchment wetness to the size of the UAA that actively contributes water to the stream. While these relationships have not been explored in our study area, they do suggest that hillslope area alone may not be a good predictor of lateral inputs. Also, lateral inputs are temporally dynamic. *McGuire and McDonnell* [2010] examined lateral inputs from a 250 m^2 planar hillslope in the nearby watershed WS10. Hillslope inputs were minimal before storms, increased rapidly after the onset of the storm, and returned to the prestorm condition within a few days of the end of the storm. The hillslopes draining directly into the valley floor within our study reach are composed of numerous segments that include tiny interfluves, planar slopes, and convergent hollows, with UAAs ranging from 17 to 305 m^2 ($\bar{X} = 110$ m^2), so results of *McGuire and McDonnell* are relevant to our study site. Given that areal-based estimates of lateral inputs are uncertain, we examine direct observations of water table height in our well network for evidence of a seasonal shift in the source and quantity of water flowing through the floodplain.

5.1.2. Water Table Shape and Lateral Inputs

Previous studies conducted in the WS1 well network strongly suggest that during summer base flow hyporheic exchange through the valley floor is little influenced by lateral inputs [*Kasahara and Wondzell*, 2003; *Wondzell*, 2006]. The water table slopes steeply down valley and is generally not elevated along the valley margin, which would be expected if lateral inputs contributed a substantial portion of the down valley flow. Further, groundwater flow model simulations fit the observed head data well when the valley margins are treated as no flow boundaries. These earlier results are all consistent with our hillslope contributing area analysis for summer base flow. All evidence shows that hillslopes adjacent to our study reach are hydrologically disconnected from the hyporheic zone during late summer.

Intensive studies of the site have not been conducted in midwinter. Rather, studies examining the relationship between catchment wetness, stream discharge, and the hyporheic zone have focused on the period of base flow recession, starting in late spring or early summer. These studies span a wide range of stream discharges, from >35 l/s to <1.0 l/s, and include a moderate-sized storm. Both direct observations from the well network [*Voltz et al*., 2013] and stream tracer injections [*Wondzell*, 2006; *Ward et al*., 2012] showed that the height and overall shape of the water table changed very little across this range of stream discharges. Even during the sampled storms, the flow paths remained strongly down valley instead of turning toward the stream [*Voltz et al*., 2013] as would be expected if storm flow conditions greatly increased lateral inputs. *Ward et al*. [2016] do see some evidence for changes in travel times to wells located furthest from the stream at extreme low flows, but conclude that “the observed changes are inconsistent with those expected where lateral inputs are the primary control on tracer arrival times” [*Ward et al*., 2016, pg. 1492]. Our 2013–2014 measurements of water table heights, collected from the well network prior to sampling, showed the same trends. That is, the shape of the water table at base flow did not change substantially over the course of our study, from extreme low flows at the end of the summer dry period through winter base flows well into the rainy season.

If the simple contributing area analysis is correct, then at winter base flow, lateral inputs should become a major source of water to the hyporheic zone. Sizable lateral inputs should either increase the amount of water flowing through the hyporheic zone (concomitantly increasing the saturated thickness of the aquifer) or they should change the direction of dominant flow paths, forcing flow laterally toward the stream and displacing stream source water. Either way, large increases in lateral inflows should have a measureable effect on the shape of the water table. Changes in the shape of the water table were not observed, even though the well network was dense, with six transects of 7 wells spanning the 14 m wide valley floor over a reach length of 29 m. The wells were located on the stream banks, in the midvalley floor, and at the toeslopes of the adjacent hillslopes. If the shape of the water table varied substantially, that change should be observable in this well network. Instead, multiple studies have repeatedly shown that the hyporheic flow net in WS1 is insensitive to changes in catchment wetness and stream discharge.

We do not mean to imply that lateral inputs are entirely lacking. Rather, the data clearly show that lateral inputs are too small to significantly alter the hydrologic flow net within the valley floor. Water chemistry, however, is quite dilute and would be sensitive to small lateral inputs, especially if DOC or DIC were highly concentrated in inflows of hillslope soil water or ground water. We examine this possibility through end-member mixing analysis.

5.1.3. End-Member Mixing Analysis

The objective of the EMMA was to look for evidence that the changes in DOC and DIC concentrations might best be explained by mixing of different source waters. We further limit the objective of the EMMA because the observed spatial patterns of DOC and DIC indicate that lateral inputs of water with relatively high DOC concentrations cannot be influencing carbon chemistry within the floodplain. If the hillslopes were an important source of DOC, then we would expect to find high concentrations on the margins of the floodplain, adjacent to the hillslopes. This was not observed. Rather, DOC is negatively correlated with distance from the stream—that is, concentrations are lower in samples collected closer to the base of the hillslopes. Thus, we use the EMMA to examine the question: “Do lateral inputs of long-residence time groundwater supply DOC-poor, and DIC-rich, water to the floodplain margins and thus explain the observed spatial patterns in carbon chemistry within the WS1 well network?”

Deep seepage to bedrock aquifers has been shown to be an important component of the water balance in nearby headwater catchments [*Graham et al*., 2010], with transient groundwater flowing along the soil-bedrock interface and through the upper bedrock via shallow networks of fractures during and immediately after storms [*Gabrielli et al*., 2012]. Deeper fracture systems also support lateral flow with much longer flow paths [*Gabrielli et al*., 2012] and median water residence times ranging from 1 to 2 years in nearby watersheds of similar size and topography [*McGuire et al*., 2005]. The source and residence time of water within the watershed should have a strong influence on the concentrations of DOC, DIC, and other solutes. We expect that soil water sources would have low concentrations of cation species because of relatively short residence times and because soil minerals are already highly weathered. Conversely, in long-residence time water, we expect that DOC should have been metabolized to DIC [*Shibata et al*., 2001] and that long contact times with bedrock would lead to the accumulation of cations through mineral weathering. Thus, we expect that deep groundwater would be relatively high in DIC and base cations, and could potentially be a source of DIC to the hyporheic zone.

The EMMA showed seasonal patterns in WS1 stream water chemistry. Concentrations of base cations in stream water were dilute from the middle through the end of the rainy season, after which the watershed dried out, discharge declined, and concentrations of major cations increased. These large shifts in the location of monthly means of stream water along PC1 suggest that the relative contribution of short and long-residence time water varies seasonally. Long-residence time groundwater dominates streamflow chemistry during summer base flow, while short-residence time soil water is proportionally more important during winter base flow when soils within the watershed are wet. We can use these seasonal patterns in stream water chemistry to examine potential spatial and temporal variation in water sources within the well network. These seasonal patterns are illustrated with data collected in September and November (Figure 5b) in order to contrast dry, late-summer conditions with wet early winter conditions.

We observed considerable variation along PC1 in both September and November when well water samples were plotted in the "U" space defined by stream water chemistry (Figure 5b). We do not see evidence for long-residence time groundwater within the well network, however, because none of the well water samples plot to the right of the stream water value, which would occur if water samples had high concentrations of base cations. Rather, most well water samples cluster close to stream water, with a small number plotting to the left of stream water. In these samples, concentrations of base cations are lower than in stream water, indicating that they likely have some proportion of short-residence time water mixed with stream water. If this potential mixing of different source waters influenced concentrations of either DOC or DIC, then we would expect to see a high correlation between DOC and/or DIC and PC1, as well as a parameter estimate (for slope) significantly different from zero in regression analysis. This was not observed (Figure 6), despite substantial variation in both DIC concentrations and scores of samples on PC1 among the wells (Figure 5b). Instead, regression analysis showed that concentrations of both DOC and DIC were more highly correlated to measures of travel time, distance from the stream, and the depth of the overlying unsaturated soil than to PC1.

The overall objective of the EMMA was to look for evidence that the changes in DOC and DIC concentrations observed within the well network on any given sample date could be better explained by mixing of water from different sources than by biogeochemical reactions that occur along flow paths through the hyporheic zone. However, we find no evidence that mixing of stream source water with long-residence time groundwater (low in DOC but high in DIC), or lateral inputs of soil water (relatively high in DOC), can explain spatial variations in the concentrations of either DOC or DIC, despite the fact that the well network spans the full valley floor, with some wells located in the wetted streambed or on streambanks with very short travel times from the stream and other wells located relatively far from the stream, at the slope break between the floodplain and the toe of the adjacent hillslope.

Collectively, neither EMMA nor the well network chemistry, nor the physical hydrology, provide convincing evidence that mixing of deep groundwater or soil water from the adjacent hillslopes are important controls on the spatial patterns of either DOC or DIC observed within our well network. Instead, the strong correlations between the concentrations of DOC and DIC with both travel time and distance from the stream suggest that in situ biogeochemical processes are the most important controls on the cycling of carbon within the hyporheic zone.

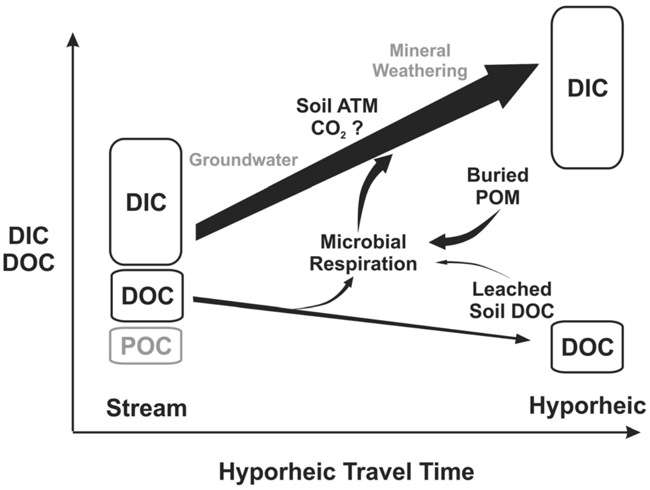

Figure 8. Conceptual model of key sources of DOC and DIC to the hyporheic zone and of transformations. Arrows are roughly proportional to the magnitude of the flux or transformation; items in gray text are potentially important in some systems, but have been shown to be unimportant in WS1.

5.2. Floodplain and Hyporheic Processes

5.2.1. Changes in DOC and DIC Along Hyporheic Flow Paths

Previous research on gravel bar hyporheic systems demonstrated strong relationships between travel time and either source-sink nitrate dynamics [*Zarnetske et al.*, 2011] or patterns of carbon metabolism [*Findlay et al.*, 1993; *Jones et al.*, 1995; *Sobczak and Findlay*, 2002]. The latter were further linked to consumption of stream-derived organic carbon along hyporheic flow paths, leading to depletion of dissolved oxygen concentrations and, in the case of *Findlay et al.* [1993], production of DIC. We examined relationships between concentrations of DIC, DOC, and travel time in order to investigate the influence of in situ biogeochemical processes on the concentrations of DIC and DOC observed in the well network (Figure 8).

Our results showed that DOC concentrations decreased, and DIC concentrations increased, with increasing nominal travel time (Figures 7a and 7b), suggesting that subsurface microbial communities could be metabolizing stream-source DOC and respiring CO_2 [*Findlay et al.*, 1993]. However, the increase in DIC with residence time was approximately 10 times larger than the decrease in DOC, and thus cannot be solely explained by the conversion of stream-source DOC (Figure 5d). This suggests that there must be additional sources of DIC and/or DOC in the subsurface, and that hyporheic DIC concentrations are not strongly linked to stream water source DOC.

Findlay et al. [1993] used concurrent measurements of dissolved oxygen (DO), DOC, and DIC to show that DIC production in the hyporheic zone was due in equal parts to metabolism of stream-source DOC and subsurface particulate organic matter. Although we did not measure DO during our study, in July 2014 the DO concentration in the WS1 stream water was measured as 8.6 mg/L (0.27 m*M*) and the lowest observed concentration within the well network was 2 mg/L (0.06 m*M*) (Serchan, unpublished data). The 6.6 mg/L (0.2 m*M*) difference between these DO concentrations would be sufficient to metabolize 0.2 m*M* (2.5 mg/L) of DOC, producing 0.2 m*M* (2.5 mg/L) of DIC, assuming that DOC and DO are consumed and DIC produced in 1:1 molar ratios [*Sobczak and Findlay*, 2002]. During summer 2013 base flow, concentrations of DOC in stream water ranged from 0.04 to 0.06 m*M*, which is far too low to account for losses of DO in the 0.2 m*M* range, whereas DIC increases along the longest flow paths range from 0.2 to 0.4 m*M*. Thus, a source of organic carbon other than DOC in stream water would be necessary to account for observed increases in DIC. It is also possible that an additional source of DIC is present, which could explain why the observed production of DIC can exceed the amount that can be accounted for by losses of DO by a factor of 2.

5.2.2. The Role of Buried Particulate Organic Carbon

Microbial respiration in hyporheic sediments under aerobic and anaerobic conditions has long been recognized as an important contributor to community respiration in stream ecosystems [*Grimm and Fisher*, 1984; *Findlay et al.*, 1993; *Pusch*, 1996; *Mulholland et al.*, 1997; *Boulton and Foster*, 1998; *Battin et al.*, 2003]. Previous studies of unvegetated gravel bar hyporheic systems have documented consumption of DOC and O_2 and production of DIC along hyporheic flow paths, and have suggested that inputs of stream-source DOC support 50–85% of heterotrophic respiration in these environments [*Findlay et al.*, 1993; *Jones et al.*, 1995; *Sobczak and Findlay*, 2002; *Zarnetske et al.*, 2011]. In WS1, a more complex riparian environment, we observed accumulations of DIC with increasing travel times, but stream-source DOC can only account for approximately 10% of the observed increase in DIC. This suggests that in hyporheic environments within forested riparian areas the dynamics of carbon processing are more complex than in gravel bar systems, and are linked through exchange of water and solutes not only to the stream itself, but also to the surrounding riparian ecosystem.

The observed increase in DIC is of similar magnitude to the observed decreases in DO, suggesting that POC buried in hyporheic sediment may be fueling microbial metabolism. We know that logs and other large particulate organic matter are buried in the sediment of the hyporheic zone and these are an obvious source of organic carbon to fuel microbial respiration [*Pusch*, 1996; *Sobczak et al*., 1998]. We do not observe consistent increases in DOC with travel time (Figure 5b). Nonetheless, there is substantial spatial variation in DOC concentrations, even in late summer, after long rain-free periods, when we would not expect vertical drainage of water through the overlying soil into the hyporheic zone. Thus it is unlikely that the overlying soil can account for this spatial variability. Instead, we suggest that this variability should be expected in a spatially heterogeneous system with buried pockets of organic matter, where microbial activity could generate DOC [*Findlay et al*., 1993; *Sobczak et al*., 1998]. Subsequent respiration of this DOC could account for the increases in DIC observed with hyporheic travel time.

5.2.3. Stream-Source Particulate Organic Carbon

Stream-source POC is another potential source of organic carbon fueling hyporheic respiration [*Pusch*, 1996]. In small headwater mountain streams like WS1, inputs of terrestrial allochthonous material are the primary source of organic material to aquatic ecosystems, and can generate fine particulate organic carbon that could be transported into the hyporheic zone. We collected unfiltered water samples during two wet season base flow periods. These point measurements indicated that POC in the stream water was below detection limits or present only in very small amounts. Of course, most stream transport of POC would occur during storms and we do not know how much of this POC would be transported into the hyporheic zone. However, for it to be an important source of organic carbon along hyporheic flow paths it must be transported long distances within the subsurface. Further, sufficient quantities of the POC entering the hyporheic zone during fall or winter storms would have to persist for long time periods in order to fuel hyporheic respiration and thereby account for the accumulation of DIC that is observed throughout the long summer base flow period.

5.2.4. Vertical Infiltration

Under wet conditions vertical drainage through the unsaturated riparian soil represents a possible source of water and solutes to the hyporheic zone [*Fiebig et al*., 1990; *Baker et al*., 1999]. This linkage would be strongest during storm events, but given very long residence times of stream water in the hyporheic zone, DOC inputs from water draining freely through the overlying soil might persist into base flow periods between storms during the wet fall and winter months. Thus, vertical infiltration may serve as a pathway to transport DOC leached from fallen leaf litter and soil organic matter into hyporheic flow paths. The EMMA provides support for this hypothesis.

The seasonal changes in stream water chemistry, when plotted in U-space, show a counterclockwise hysteresis, becoming positive along PC2 in late fall and early winter and negative in late spring and early summer. Chloride is the only solute with strongly positive weightings on this axis; Ca^{+2}, Mg^{+2}, and Na^{+} all plot near zero on PC2, so clearly this pattern is controlled by observed changes in the concentration of Cl^{-} in stream water. Similar seasonal changes in the concentrations of Cl^{-} in stream water were observed by *van Verseveld et al*. [2008] in the nearby watershed, WS10. While precipitation chemistry also shows counterclockwise hysteresis, seasonal changes in the concentrations of Cl^{-} in precipitation cannot explain the trends observed in stream water. First, Cl^{-} is nearly always more dilute in rainfall than in stream water (Figures 3b and 5a). Second, very little rain falls from May through September and thus, summer rains cannot “dilute” Cl^{-} concentrations in stream water.

Leaching of shallow soils with the onset of the rainy season can explain the increased stream and hyporheic concentrations of Cl^{-} in fall and early winter. We suggest that Cl^{-} may become concentrated within the shallow soil during the summer due to either direct evaporation of water from the surface soil or decomposition of plant litter in which Cl^{-} has become concentrated through transpiration. Both processes would tend to store Cl^{-} near the soil surface because summers are typically dry with little precipitation from late June through September. With the onset of the rainy season, this Cl^{-} would be leached from the soil, resulting in elevated concentrations of Cl^{-} in hyporheic and stream water for the first few months of the rainy season, as was observed. In the hyporheic wells in November concentrations of DOC were elevated, and were highly correlated with PC2. In this winter-rain dominated environment, repeated flushing would be expected to deplete soil water concentrations of mobile solutes, leading concentrations in stream and hyporheic water to be low for the remainder of the year. We did observe lower concentrations of DOC and Cl^- in December and March than in November (Figures 4a and 4b).

While vertical leaching could be a source of DOC, the rate of DOC inputs from the overlying soil must be much smaller than the rate at which DOC is metabolized along these flow paths, because DOC concentrations were almost always lower in the hyporheic zone than in stream water during the base flow periods we sampled (Figures 7a and 7b).

5.2.5. Interactions Between the Soil Atmosphere and the Hyporheic Zone

Carbon dioxide from the overlying soil could also be an important source of DIC to the WS1 hyporheic zone [*Shibata et al.*, 2001; *Butman and Raymond*, 2011; *Tsypin and Macpherson*, 2012]. Decomposition of soil organic matter and root respiration generate high concentrations of CO_2 in the soil atmosphere [*Sulzman et al.*, 2005], which could diffuse or advect across the water table. Diffusion is a slow process, however. The aqueous diffusion coefficient for the dominant DIC species in WS1, HCO_3^-, is 7.3×10^{-10} m^2/s at 10°C [*Zeebe*, 2011], so it can only diffuse approximately 1 cm every 38 h. Thus advection is likely needed to transport substantial quantities of CO_2 into the hyporheic zone.

The water table is not a simple, planar-free water surface. Rather, the saturated and vadose zones grade together through a capillary fringe, which creates a large air-water interface across which diffusion can take place. Further, the height of the water table fluctuates—during summer base flow, evapotranspiration drives diel fluctuations of several centimeters [*Wondzell et al.*, 2007, 2010], which would cause the capillary fringe to extend higher into the soil profile as the water table rises over the diel cycle. This water must drain back into the hyporheic zone as the water table falls. Vertical drainage of water through the soil, or small fluctuations in water table height over storm cycles, would work similarly in the wet season. This mechanism could transport soil-source DIC and other soil gases into hyporheic water [*Williams and Oostrom*, 2000; *Thaysen et al.*, 2014], and appears to be more effective in heterogeneous media than in homogenous media [*Haberer et al.*, 2015]. We have not quantified these mechanisms, thus we do not know their importance to carbon fluxes in the WS1 hyporheic zone. However, these mechanisms provide obvious sources of DIC and could account for concentrations exceeding the amount that could be generated through microbial respiration given the potential changes in dissolved oxygen.

5.2.6. Mineral Weathering as a Source of DIC

Another potential source of DIC to the hyporheic zone is the production of bicarbonate through mineral weathering of carbonates [*Findlay et al.*, 1993]. No carbonates are present in regional bedrock [*Swanson and James*, 1975], thus hydrolysis of carbonate minerals is not a plausible source of DIC. This conclusion is supported by strong correlations between DIC and pH in all sampling months (Figure 7c), which indicate that CO_2 is the primary source of DIC to WS1 hyporheic waters. While mineral weathering is unimportant at our study site, this source of DIC might be expected in locations with carbonate-rich parent materials.

5.2.7. Adsorption and Desorption

Adsorption of DOC to clays and iron and aluminum oxides can be a potentially important mechanism for DOC removal from water moving through soils [*McDowell*, 1985; *Findlay et al.*, 1993; *Liu et al.*, 2014]. Adsorption is greater under oxic conditions and at low pH [*Liu et al.*, 2014]. We did not measure iron or aluminum concentrations, but the pH of hyporheic water ranges from 6 to 7 and point measurements indicate that hyporheic water is generally oxic (Serchan, unpublished data, 2014). Adsorption may therefore be a mechanism for DOC removal in the hyporheic zone of WS1. Desorption of adsorbed DOC would reverse this process, and could in turn represent a source of DOC to hyporheic microbes. DOC may also be removed and stored in subsurface biofilms through biological uptake [*Battin*, 1999]. Eventually, this stored DOC may be metabolized, producing DIC. It is difficult to constrain the magnitude and timescale of these processes of DOC removal and cycling. However, the observed accumulation of DIC along subsurface flow paths within WS1 suggests that the loss of DOC via adsorption or storage is unimportant in comparison to biotic consumption of DOC [*Findlay et al.*, 1993].

5.3. Impact of HZ on Stream Carbon and Whole-Watershed Exports

5.3.1. The Role of Spatial Intermittency

The very low concentrations of DOC in the stream water ($\bar{x} = 0.82$, range 0.54–1.13 mg/L) are likely explained by metabolic consumption of DOC during hyporheic exchange. Concentrations of DOC in hyporheic flow paths are almost always lower than the stream ($\bar{x} = 0.67$, range 0.18–1.20 mg/L; Figure 7a) and estimates from groundwater flow models of the study reach indicate that, during low base flow periods in late summer, 76% of streamflow would pass through the hyporheic zone along a 100 m reach of WS1

[*Kasahara and Wondzell*, 2003]. As a consequence, the entire stream discharge passes through the hyporheic zone multiple times before reaching our well network, so that most solutes in the stream water would already have been repeatedly exposed to hyporheic processes. Assuming that hyporheic zones upstream are similar to the one in our study reach, then hyporheic exchange should drive a continual loss of DOC along the length of the stream network. The stream becomes spatially intermittent by midsummer, upstream of our study reach, with numerous dry reaches. By late summer the wetted channel extends only ~75 m above our well network. Thus, the products of autochthonous, or in-stream, processes can accumulate only over a very short distance, so that the opportunity for DOC accumulation in the stream water is likely small, while losses from heterotrophic metabolism in the hyporheic zone are likely large. Together, these factors would explain the low concentrations of DOC.

The high rates of hyporheic exchange and the spatially intermittent flow structure amplify the influence of subsurface carbon processing on stream water chemistry. Hyporheic return flows import large quantities of DIC to the stream, but low flows limit turbulence and wetted reach lengths are relatively short, restricting the evasion of CO_2. As a result, surface water reaching the well network is low in DOC, enriched in DIC, and increasingly supersaturated in CO_2 [*Dosch*, 2014], as was observed in summer 2013 (Figures 4a and 4c). With the onset of the rainy season in late September and early October, surface flow in WS1 once again becomes continuous and remains so until the following summer. When this occurs, spatial intermittency no longer controls the physical movement of water in WS1, and a smaller proportion of total discharge passes through the hyporheic zone. This lessens the exposure of stream water to microbial communities, diminishing the influx of DIC-rich water to the stream via subsurface pathways. *Dosch* [2014] observed that the partial pressure of dissolved CO_2 within the study reach, which had increased steadily throughout the dry season, decreased dramatically at the end of September 2013 when the first large rainstorm occurred. Because of this physical-biogeochemical dynamic, we suggest that spatial intermittency is an important seasonal driver of carbon processing in WS1.

5.3.2. Buried Organic Matter

Both stream water and hyporheic zone water were supersaturated with CO_2 with respect to the atmosphere [*Dosch*, 2014]. Data presented here suggest that a critical source for this DIC is the metabolic processing of buried particulate organic carbon. In this landslide prone, forested landscape, the valley-floor sediment of high-gradient streams is deposited by debris flows. These debris flows transport both mineral sediment and a variety of organic materials ranging in size from small organic particles to large logs. Debris flows tend to sort particles by size and density such that large logs are preferentially transported at the front of the debris flow. However, when these logs become wedged in narrow reaches of the valley they obstruct the debris flow, causing sediment deposition, and can themselves be buried by sediment. Debris flows tend to mix finer organic and mineral sediment so that organic matter is mixed throughout the debris flow deposits. The resulting colluvium that comprises the floodplain sediment is relatively rich in organic matter and the large logs buried in this sediment will persist for long periods.

Floodplains are important locations for organic matter storage in many locations [*Sutfin et al*., 2016]. For example, in large floodplain rivers, floods transport and bury large amounts of organic matter [*Robertson et al*., 1999] and bury organic soil horizons in situ [*Gurwick et al*., 2008]. In many smaller rivers, beaver dams lead to the deposition of organic rich sediment in the pond upstream of the dam [*Wohl et al*., 2012]. *Wohl et al*. [2012] estimated that 25% of the carbon stored in a mountainous watershed characterized by dry, subalpine forest was located within the riparian zone, even though the riparian zone only accounted for 1% of the watershed area.

We suggest that hyporheic exchange is an important mechanism facilitating the biogeochemical transformation of particulate organic carbon buried in the floodplains of mountain stream networks (Figure 8). First, stream water supplies dissolved O_2 to the hyporheic zone where heterotrophic activity tends to be dominated by aerobic respiration [*Pusch*, 1996; *Mermillod-Blondin et al*., 2005], at least in part because aerobic respiration rates are greater than anaerobic respiration rates [*DeBusk and Reddy*, 1998]. Thus, the supply of O_2 might be a critical limitation on the rate at which buried POC is metabolized in mountain streams, especially in streams where other terminal electron acceptors, such as NO_3^- or SO_4^-, are present in relatively low concentrations in stream and hyporheic waters. Second, hyporheic exchange provides a mechanism to transport CO_2 from the floodplain to the stream where it can be evaded to the atmosphere or transported downstream. Estimates for WS1 suggest that these hyporheic processes account for 24% of the carbon exported from the watershed [*Argerich et al*., 2016].

6. Conclusions

We investigated the influence of hyporheic processing and mixing of different source waters on the dynamics of DOC consumption and DIC production in a forested headwater mountain stream. We studied this system during base flow discharge over a 9 month period, capturing a seasonal shift from dry summer conditions to the wet fall and winter months. We did not find convincing evidence that either inputs of deep groundwater or lateral inputs of shallow soil water influenced carbon dynamics. Rather, all evidence suggests that the hyporheic zone is disconnected from hillslope and groundwater systems during base flow, both during dry periods in late summer as well as during wet midwinter periods. Thus, carbon dynamics appear to be controlled by local processes in the hyporheic zone and overlying riparian soils. Concentrations of DOC decreased as both distance from the stream and the nominal travel time to individual wells increased; concentrations of DIC increased over this same distance. Increases in DIC, however, were approximately 10-fold larger than the amount of stream-source DOC entering the hyporheic zone on all monthly sample dates, thus DOC in stream water can only account for 10% of the observed increase in DIC. In situ metabolic processes appear to account for a large portion of the increase in DIC and buried particulate organic matter is the most likely source of organic carbon for microbial metabolism. Observed increases in DIC were sometimes larger than would be expected from complete utilization of all O_2 entering the hyporheic zone in the stream water, suggesting that a nonmetabolic source contributes DIC to the hyporheic water. The most likely source of this DIC is the vadose zone of the overlying soil, where CO_2 is likely present in high concentrations within the soil gases. Overall, the hyporheic zone was a source of DIC to the stream. We suggest that in mountain stream networks hyporheic exchange facilitates the transformation of particulate organic carbon buried in floodplains and transports the DIC that is produced back to the stream where it can be evaded to the atmosphere.

Acknowledgments

Following publication, all data will be made available through the H.J. Andrews Experimental Forest data catalog, which can be accessed via the following url: http://andrewsforest.oregonstate.edu/lter/data.cfm?frameURL=8. We also cited unpublished data collected by Serchan and Pennington. Satish Serchan can be reached at satish.serchan@gmail.com, and Robert Pennington can be reached at robertopennington@gmail.com. Direct support for this work was provided by agreement 10-JV-11261991-055-PNW. Additional funding and support for this research was provided by the U.S. Forest Service Pacific Northwest Research Station, the Water Resources Graduate Program, the Oregon State University Provost's Distinguished Fellowship, and the National Science Foundation (EAR 1417603). Data and research facilities were provided by the H.J. Andrews Experimental Forest research program, which is funded by the National Science Foundation's Long-Term Ecological Research Program (DEB 0823380), the U.S. Forest Service Pacific Northwest Research Station, and Oregon State University. We thank Nick Dosch for help with fieldwork, Lisa Ganio for help with data analysis, Noah Schmadel and Adam Ward who provided analyses of watershed drainage areas and UAA, both the H.J. Andrews staff and the LTER research network for data and field support, and the IWW Collaboratory and Kathy Motter for laboratory equipment and training, as well as technical support.

References

Argerich, A., R. Haggerty, S. L. Johnson, S. M. Wondzell, N. Dosch, H. Corson-Rikert, L. R. Ashkenas, R. Pennington, and C. K. Thomas (2016), Comprehensive multiyear carbon budget of a temperature headwater stream, *J. Geophys. Res. Biogeosci.*, *121*, 1306–1315, doi:10.1002/2015JG003050.

Baker, M. A., C. N. Dahm, and H. M. Valett (1999), Acetate retention and metabolism in the hyporheic zone of a mountain stream, *Limnol. Oceanogr.*, *44*(6), 1530–1539, doi:10.4319/lo.1999.44.6.1530.

Battin, T. J. (1999), Hydrologic flow paths control dissolved organic carbon fluxes and metabolism in an alpine stream hyporheic zone, *Water Resour. Res.*, *35*(10), 3159–3169.

Battin, T. J., L. A. Kaplan, D. J. Newbold, and S. P. Hendricks (2003), A mixing model analysis of stream solute dynamics and the contribution of a hyporheic zone to ecosystem function, *Freshwater Biol.*, *48*, 995–1014.

Battin, T. J., L. A. Kaplan, S. Findlay, C. S. Hopkinson, E. Marti, A. I. Packman, J. D. Newbold, and F. Sabater (2008), Biophysical controls on organic carbon fluxes in fluvial networks, *Nat. Geosci.*, *1*, 95–100, doi:10.1038/ngeo602.

Boulton, A. J., and J. G. Foster (1998), Effects of buried leaf litter and vertical hydrologic exchange on hyporheic water chemistry and fauna in a gravel-bed river in northern New South Wales, Australia, *Freshwater Biol.*, *40*(2), 229–243.

Butman, D., and P. A. Raymond (2011), Significant efflux of carbon dioxide from streams and rivers in the United States, *Nat. Geosci.*, *4*, 839–842, doi:10.1038/ngeo1294.

CCAL (2013), CCAL Standard Operating Procedures, Oreg. State Univ. and U.S. For. Serv. Coop. Chem. Anal. Lab., Corvallis, Oreg. [Available at http://ccal.oregonstate.edu/sops, accessed June 2013.]

Christophersen, N., and R. Hooper (1992), Multivariate analysis of stream water chemical data: The use of principal components analysis for the end-member mixing problem, *Water Resour. Res.*, *28*(1), 99–107.

Cole, J. J., and N. F. Caraco (2001), Carbon in catchments: Connecting terrestrial carbon losses with aquatic metabolism, *Mar. Freshwater Res.*, *52*, 101–110, doi:10.1071/MF00084.

Corson-Rikert, H. A. (2014), Carbon dynamics in the hyporheic zone of a headwater mountain stream in the Cascade Mountains, Oregon, MS thesis, Oreg. State Univ., Corvallis. [Available at http://hdl.handle.net/1957/52356.]

DeBusk, W. F. and K. R. Reddy (1998), Turnover of detrital organic carbon in a nutrient-impacted everglades marsh, *Soil Sci. Soc. Am. J.*, *62*(5), 1460–1468, *doi:10.2136/sssaj1998.03615995006200050045x*.

Dosch, N. T. (2014), Spatiotemporal dynamics and drivers of stream pCO_2 in a headwater mountain catchment in the Cascade Mountains, Oregon, MS thesis, Oreg. State Univ., Corvallis. [Available at http://hdl.handle.net/1957/52410.]

Downing, J., J. J. Cole, C. M. Duarte, J. J. Middelburg, J. M. Melack, Y. T. Prairie, P. Kortelainen, R. G. Striegl, W. H. McDowell, and L. J. Tranvik (2012), Global abundance and size distribution of streams and rivers, *Inland Waters*, *2*, 229–236, doi:10.5268/IW-2.4.502.

Fiebig, D. M., M. A. Lock, and C. Neal (1990), Soil water in the riparian zone as a source of carbon for a headwater stream, *J. Hydrol.*, *166*, 217–237, doi:10.1016/0022-1694(90)90124-G.

Findlay, S., D. Strayer, C. Goumbala, and K. Gould (1993), Metabolism of streamwater dissolved organic carbon in the shallow hyporheic zone, *Limnol. Oceanogr.*, *38*(7), 1493–1499, doi:10.4319/lo.1993.38.7.1493.

Gabrielli, C. P., J. J. McDonnell, and W. T. Jarvis (2012), The role of bedrock groundwater in rainfall–runoff response at hillslope and catchment scales, *J. Hydrol.*, *450-451*, 117–133, doi:10.1016/j.jhydrol.2012.05.023.

Graham, C. B., W. van Verseveld, H. R. Barnard, and J. J. McDonnell (2010), Estimating the deep seepage component of the hillslope and catchment water balance within a measurement uncertainty framework, *Hydrol. Processes*, *24*(25), 3631–3647, doi:10.1002/hyp.7788.

Grimm, N. B., and S. G. Fisher (1984), Exchange between interstitial and surface water: Implications for stream metabolism and nutrient cycling, *Hydrobiologia*, *111*, 219–228.

Gurwick, N. P., P. M. Groffman, J. B. Yavitt, A. J. Gold, G. Blazejewski, and M. Stolt (2008), Microbially available carbon in buried riparian soils in a glaciated landscape, *Soil. Biol. Biochem.*, *40*(1), 85–96, doi:10.1016/j.soilbio.2007.07.007.

Haberer, C. M., M. Rolle, O. A. Cirpka, and P. Grathwohl (2015), Impact of heterogeneity on oxygen transfer in a fluctuating capillary fringe, *Groundwater*, *53*(1), 57–70.

Halpern, C. B., and J. F. Franklin (1990), Physiognomic development of Pseudotsuga forests in relation to initial structure and disturbance intensity, *J. Veg. Sci.*, *1*, 475–482.

Hooper, R. P. (2003), Diagnostic tools for mixing models of stream water chemistry, *Water Resour. Res.*, *39*(3), 1055, doi:10.1029/2002WR001528.

Inamdar, S., S. Singh, S. Dutta, D. Levia, M. Mitchell, D. Scott, H. Bais, and P. McHale (2011), Fluorescence characteristics and sources of dissolved organic matter for stream water during storm events in a forested mid-Atlantic watershed, *J. Geophys. Res.*, *116*, G03043, doi:10.1029/2011JG001735.

Jencso, K. G., B. L. McGlynn, M. N. Gooseff, S. M. Wondzell, K. E. Bencala, and L. A. Marshall (2009), Hydrologic connectivity between landscapes and streams: Transferring reach and plot-scale understanding to the catchment scale, *Water Resour. Res.*, *45*, W04428, doi:10.1029/2008WR007225.

Johnson, S. L., and R. L. Fredriksen (2015), Stream chemistry concentrations and fluxes using proportional sampling in the Andrews Experimental Forest, 1968 to present. Long-Term Ecological Research. For. Sci. Data Bank, Corvallis, Oreg. [Available at http://andrewsforest.oregonstate.edu/data/abstract.cfm?dbcode=CF002, last accessed on 13 Sep 2015.]

Johnson, S. L., and J. A. Jones (2000), Stream temperature responses to forest harvest and debris flows in western Cascades, Oregon, *Can. J. Fish. Aquat. Sci.*, *57*(S2), 30–39, doi:10.1139/cjfas-57-S2-30.

Jones, J. B., S. G. Fisher, and N. B. Grimm (1995), Vertical hydrologic exchange and ecosystem metabolism in a Sonoran desert stream, *Ecology*, *76*(3), 942–952.

Kasahara, T. (2000), Geomorphic controls on hyporheic exchange flow in mountain streams, MS thesis, 103 p., Oreg. State Univ., Corvallis.

Kasahara, T., and S. M. Wondzell (2003), Geomorphic controls on hyporheic exchange flow in mountain streams, *Water Resour. Res.*, *39*(1), 1005, doi:10.1029/2002WR001386.

Levno, A., and J. Rothacher (1969), Increases in maximum stream temperatures after slash burning in a small experimental watershed, *PNW-11*, 7 pp., Pac. Northwest For. and Range Exp. Stn., U.S.D.A. For. Serv., Corvallis, Oreg.

Liu, W., X. Xu, N. M. McGoff, J. M. Eaton, P. Leahy, N. Foley, and G. Kiely (2014), Spatial and seasonal variation of dissolved organic carbon (DOC) concentrations in Irish streams: Importance of soil and topography characteristics, *Environ. Manage.*, *53*(5), 959–67, doi:10.1007/s00267-014-0259-1.

McDowell, W. H. (1985), Kinetics and mechanisms of dissolved organic carbon retention in a headwater stream, *Biogeochemistry*, *1*(4), 329–352.

McGlynn, B. L., and J. J. McDonnell (2003), Role of discrete landscape units in controlling catchment dissolved organic carbon dynamics, *Water Resour. Res.*, *39*(4), 1090, doi:10.1029/2002WR001525.

McGuire, K. J., and J. J. McDonnell (2010), Hydrological connectivity of hillslopes and streams: Characteristic time scales and nonlinearities, *Water Resour. Res.*, *46*, W10543, doi:10.1029/2010WR009341.

McGuire, K. J., J. J. McDonnell, M. Weiler, C. Kendall, B. L. McGlynn, J. M. Welker, and J. Seibert (2005), The role of topography on catchment-scale water residence time, *Water Resour. Res.*, *41*, W05002, doi:10.1029/2004WR003657.

Mermillod-Blondin, F., L. Mauclaire, and C. Montuelle (2005), Use of slow filtration columns to assess oxygen respiration, consumption of dissolved organic carbon, nitrogen transformations, and microbial parameters in hyporheic sediments, *Water Res.*, *39*(9), 1687–1698, doi:10.1016/j.watres.2005.02.003.

Mulholland, P. J., E. R. Marzolf, J. R. Webster, D. R. Hart, and S. P. Hendricks (1997), Evidence that hyporheic zones increase heterotrophic metabolism and phosphorus uptake in forest streams, *Limnol. Oceanogr.*, *42*(3), 443–451.

Pusch, M. (1996), The metabolism of organic matter in the hyporheic zone of a mountain stream, and its spatial distribution, *Hydrobiologia*, *323*, 107–118.

Pusch, M., and J. Schwoerbel (1994), Community respiration in hyporheic sediments of a mountain stream (Steina, Black Forest), *Arch. Hydrobiol.*, *130*(1), 35–52.

Regnier, P., et al. (2013), Anthropogenic perturbation of the carbon fluxes from land to ocean, *Nat. Geosci.*, *6*, 597–607, doi:10.1038/ngeo1830.

Robertson, A. I., S. E. Bunn, P. I. Boon, and K. F. Walker (1999), Sources, sinks and transformations of organic carbon in Australian floodplain rivers, *Mar. Freshwater Res.*, *50*, 813–829, doi:10.1071/MF99112.

Rothacher, J., C. T. Dyrness, and R.L. Fredriksen (1967), *Hydrologic and Related Characteristics of Three Small Watersheds in the Oregon Cascades*, 54 pp., U.S.D.A. For. Serv., Pac. Northwest For. and Range Exp. Stn., Portland, Oreg.

Schindler, J. E., and D. P. Krabbenhoft (1998), The hyporheic zone as a source of dissolved organic carbon and carbon gases to a temperate forested stream, *Biogeochemistry*, *43*(2), 157–174.

Schwanghart, W., and N. J. Kuhn (2010), TopoToolbox: A set of Matlab functions for topographic analysis, *Environ. Modell. Software*, *25*, 770–781, doi:10.1016/j.envsoft.2009.12.002.

Seibert, J., and B. L. McGlynn (2007), A new triangular multiple flow direction algorithm for computing upslope areas from gridded digital elevation models, *Water Resour. Res.*, *43*, W04501, doi:10.1029/2006WR005128.

Shibata, H., H. Mitsuhashi, Y. Miyake, and S. Nakano (2001), Dissolved and particulate carbon dynamics in a cool-temperate forested basin in Northern Japan, *Hydrol. Processes*, *15*(10), 1817–1828, doi:10.1002/hyp.241.

Sobczak, W. V., and S. Findlay (2002), Variation in bioavailability of dissolved organic carbon among stream hyporheic flow paths, *Ecology*, *83*(11), 3194–3209.

Sobczak, W. V., L. O. Hedin, and M. J. Klug (1998), Relationships between bacterial productivity and organic carbon at a soil-stream interface, *Hydrobiologia*, *386*, 45–53, doi:10.1023/A:1003583813445.

Sulzman, E. W., J. B. Brant, R. D. Bowden, and K. Lajtha (2005), Contribution of aboveground litter, belowground litter, and rhizosphere respiration to total soil CO_2 efflux in an old growth coniferous forest, *Biogeochemistry*, *73*(1), 231–256, doi:10.1007/s10533-004-7314-6.

Sutfin, N. A., E. E. Wohl, and K. A. Dwire (2016), Banking carbon: A review of organic carbon storage and physical factors influencing retention in floodplains and riparian ecosystems, *Earth Surf. Processes Landforms*, *41*, 38–60.

Swanson, F.J., and M.E. James (1975), Geology and geomorphology of the H.J. Andrews Experimental Forest, Western Cascades, Oregon, *PNW-188*, 15 pp., Pac. Northwest For. and Range Exp. Stn., U.S.D.A. For. Serv., Corvallis, Oreg.

Thaysen, E. M., S. Jessen, P. Ambus, C. Beier, D. Postma, and I. Jakobsen (2014), Technical note: Mesocosm approach to quantify dissolved inorganic carbon percolation fluxes, *Biogeosciences*, *11*(4), 1077–1084, doi:10.5194/bg-11-1077-2014.

Tsypin, M., and G. L. Macpherson (2012), The effect of precipitation events on inorganic carbon in soil and shallow groundwater, Konza Prairie LTER Site, NE Kansas, USA, *Appl. Geochem.*, *27*, 2356–2369, doi:10.1016/j.apgeochem.2012.07.008.

van Verseveld, W. J., J. J. McDonnell, and K. Lajtha (2008), A mechanistic assessment of nutrient flushing at the catchment scale, *J. Hydrol.*, *358*, 268–287, doi:10.1016/j.jhydrol.2008.06.009.

Voltz, T., M. Gooseff, A. S. Ward, K. Singha, M. Fitzgerald, and T. Wagener (2013), Riparian hydraulic gradient and stream-groundwater exchange dynamics in steep headwater valleys, *J. Geophys. Res. Earth Surf.*, *118*, 953–969, doi:10.1002/jgrf.20074.

Ward, A. S., M. Fitzgerald, M. N. Gooseff, T. J. Voltz, A. M. Binley, and K. Singha (2012), Hydrologic and geomorphic controls on hyporheic exchange during base flow recession in a headwater mountain stream, *Water Resour. Res.*, *48*, W04513, doi:10.1029/2011WR011461.

Ward, A. S., N. M. Schmadel, S. M. Wondzell, C. Harman, M. N. Gooseff, and K. Singha (2016), Hydrogeomorphic controls on hyporheic and riparian transport in two headwater mountain streams during base flow recession, *Water Resour. Res.*, *52*, 1479–1497, doi:10.1002/2015WR018225.

Williams, M. D., and M. Oostrom (2000), Oxygenation of anoxic water in a fluctuating water table system: An experimental and numerical study, *J. Hydrol.*, *230*(1-2), 70–85, doi:10.1016/s0022-1694(00)00172-4.

Wohl, E., K. Dwire, N. Sutfin, L. Polvi, and R. Bazan (2012), Mechanisms of carbon storage in mountainous headwater rivers, *Nat. Commun.*, *3*, 1263, doi:10.1038/ncomms2274.

Wondzell, S. M. (2006), Effect of morphology and discharge on hyporheic exchange flows in two small streams in the Cascade Mountains of Oregon, USA, *Hydrol. Processes*, *20*(2), 267–287, doi:10.1002/hyp.5902.

Wondzell, S. M. (2011), The role of the hyporheic zone across stream networks, *Hydrol. Processes*, *25*(22), 3525–3532, doi:10.1002/hyp.8119.

Wondzell, S. M., M. N. Gooseff, and B. L. McGlynn (2007), Flow velocity and the hydrologic behavior of streams during base flow, *Geophys. Res. Lett.*, *34*, L24404, doi:10.1029/2007GL031256.

Wondzell, S. M., M. N. Gooseff, and B. L. McGlynn (2010), An analysis of alternative conceptual models relating hyporheic exchange flow to diel fluctuations in discharge during base flow recession, *Hydrol. Processes*, *24*, 686–694.

Zarnetske, J. P., R. Haggerty, S. M. Wondzell, and M. A. Baker (2011), Dynamics of nitrate production and removal as a function of residence time in the hyporheic zone, *J. Geophys. Res.*, *116*, G01025, doi:10.1029/2010JG001356.

Zeebe, R. E. (2011), On the molecular diffusion coefficients of dissolved CO_2, HCO^{3-}, and CO_3^{2-} and their dependence on isotopic mass, *Geochim. Cosmochim. Acta*, *75*(9), 2483–2498, doi:10.1016/j.gca.2011.02.010.