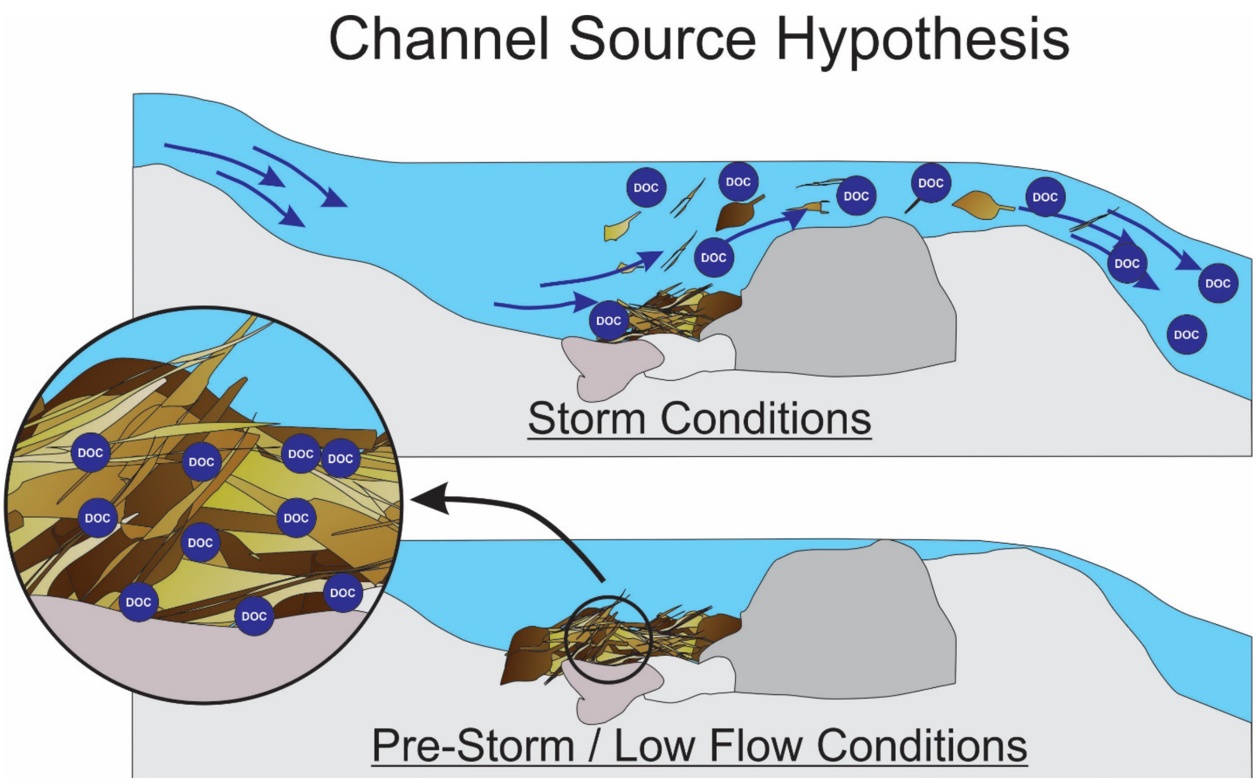
The Channel Source Hypothesis: Empirical Evidence for In-Channel Sourcing of Dissolved Organic Carbon to Explain Hysteresis in a Headwater Mountain Stream

Steven M. Wondzell* & Adam S. Ward

Organic matter from litter fall or autochthonous production is stored in dead zones within the wetted stream channel under low-flow conditions. Leaching and microbial processes generate DOC within the organic matter. As water depth and flow velocity increase during the rising leg of the storm hydrograph, organic matter can be scoured out of dead zones, releasing the accumulated DOC into the active stream channel.



The Channel Source Hypothesis: Empirical Evidence for In-Channel Sourcing of Dissolved Organic Carbon to Explain Hysteresis in a Headwater Mountain Stream

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Abstract

Catchment hydrologists have long puzzled over the question: How can catchments rapidly generate storm flows and pulses of solutes in response to storm events? Conceptual models viewing catchments as composed of discrete source areas generating flow at unique time scales and with unique chemical characteristics have been used to explain the observed changes in flow and water chemistry. Surprisingly, those conceptual models usually do not treat the stream channel as one of the potential source areas. Here, we propose the *channel source hypothesis* in which the stream itself should be considered as a potential source with the same rigor as other contributing areas. We pose this in the spirit of the scientific use of the word: a hypothesis[1] is not a proven idea but rather a provisional supposition serving as the basis for further study. We suggest that the channel should be considered as a potential source for dissolved organic carbon (DOC). Channels store substantial amounts of organic matter, and stream ecologists have long studied stream carbon cycling. From those studies we know that leaching and decomposition can generate DOC from particulate organic carbon (POC). Further, POC is stored in channel "dead-zones" - regions of low flow velocity - that can be activated as flow velocity increases, thus releasing accumulated DOC during storms. All catchments are different; there is no reason to assume that channel sources are always important, in every catchment, in every storm. Thus, the channel source hypothesis does not replace existing conceptual models. Instead, it adds another potential mechanism that may explain DOC dynamics observed in streams. The channel source hypothesis has substantial implications for catchment studies examining sources of DOC in stream water or using DOC as a tracer to determine the locations of, and proportional contributions of, different source areas for streamflow generation.

Keywords: dissolved organic carbon; storm flow; concentration-discharge relationships; headwater mountain stream.

[1] Hypothesis: "*a provisional supposition from which to draw conclusions that shall be in accordance with known facts and serves as a starting point for further investigation by which it may be proved or disproved and the true theory arrived at*" quoted from the Oxford English Dictionary (OED), 1985.

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1. INTRODUCTION

Catchment hydrology has long puzzled over the seemingly simple question: *How can catchments rapidly generate storm flows in response to storm events?* Hydrologists quickly eliminated streams and their channels from consideration because calculations based on the wetted surface area of the stream network and the amount of rainfall conclusively showed that direct channel precipitation did not contribute significantly to peak storm flows. Thus, the earliest studies turned to the catchment as a source of storm flows. In 1933, Horton proposed a simple overland flow model, in part, because subsurface flows are too slow to reach the stream and generate peak flows over short periods of time. Today, this is known as "Hortonian" or "infiltration-excess" overland flow and is well documented in locations with low rates of infiltration. In forested catchments with relatively undisturbed soils, however, infiltration rates are almost always higher than precipitation rates so that surface runoff is almost never observed. These observations challenged Horton's view, eventually leading Hewlett and Hibbert (1967) to propose a translatory flow mechanism through which increased pressure from infiltrating rainfall "pushes" water that was already stored in the soil out the bottom of the hillslope and into streams, thus providing a mechanism through which slow subsurface flows could rapidly generate peak flows. Since then, a variety of other mechanisms have been proposed (e.g., variable source areas, Dunne and Black, 1970; preferential flow, Beven, 1989; but see section 4.1 for a more complete treatment of these mechanisms).

A serious shortcoming of direct observational studies is that catchments are complex, composed of many discrete source areas (McDonnell, 2003), and direct observation cannot distinguish the relative contribution of water draining from different areas to the generation of peak flows. To solve this problem, catchment hydrologists turned to naturally occurring tracers. If these were conservative (i.e., they moved through the catchment identically to the flow of water, neither being generated, retained, nor transformed), and their concentrations were sufficiently different among end members, then they could be used to identify the relative contribution of each end member. The use of tracers led to an explosion of hydrological studies exploring the role of different end members in generating flows, not only peak flows during storms but also baseflows during long, precipitation free periods. The stable isotopes $\delta^{18}O$ and $\delta^{2}H$ are among the most conservative of potential tracers and thus ideal for this purpose. However, with only a small number of isotopes to choose from and many potential end members, additional tracers were needed. Consequently, catchment hydrologists turned to elements such as Ca, K, Mg, Na, Cl, SO_4, and Si (Barthold et al., 2011). While these might not be perfectly conservative, if they were present in sufficiently high concentrations and sufficiently distinct from other source areas, it was generally accepted that these tracers would suffice for end-member separation. Surprisingly, DOC, many forms of which are highly reactive, has also been used as a tracer because its concentrations are high in throughfall and in shallow soil flow paths, and over the short time scales of a single storm event, its behavior is thought to be sufficiently conservative to be used as a tracer.

End member mixing and hydrograph separation techniques conceptualize streams as a mixture of water from different sources, each with a unique chemical signature and a unique travel time to the stream, and the relative contribution to stream flow from each source area can vary over time (Bishop, Seibert, & Stephan, 2004). However, there is no guarantee that the resulting mixing model provides a unique solution to the sources of stream flow. In fact, the end member solution will be sensitive to the number of tracers used and the elements selected as tracers (Barthold et al., 2011), in part because the tracers are not perfectly conservative and because the relative similarities or differences in tracer concentrations among potential end members will not be uniform across all tracers. Further, it is not possible to collect a statistically representative sample of all possible end members in all locations throughout a catchment. Consequently, these analytical techniques identify potential end members, which, if mixed in different proportions, can reasonably account for the changes in stream solute concentrations over the period of study. This does not guarantee, however, that all important source areas and/or end members are included in the mixing model.

End member mixing analyses and hydrograph separation techniques are now commonly used to identify the likely source areas and flowpaths determining the whole watershed export of specific solutes and their dynamic responses during storms. For example, this approach underpins the explanation of hysteresis in streamwater DOC based on a wide range of mechanisms including sequenced delivery of water, from riparian zones early in the storm and from hillslopes late in the storm (McGlynn & McDonnell, 2003), activation of distal patches of high DOC runoff (Gannon, Bailey, McGuire, and Shanley, 2015), and rapid connection of hillslope organic horizon water to streams via preferential flow paths (van Verseveld, McDonnell, & Lajtha, 2008). While the specifics of the runoff generation mechanisms that ultimately explain observed DOC concentration-discharge dynamics vary, they all share one essential feature: DOC enrichment during storm events is always attributed to the mobilization of sources outside of the stream channel. Hydrologists are not alone in assuming sources of water and DOC must be coupled. For example, Raymond, Saiers, & Sobczak (2016) invoke pulses of DOC generated from terrestrial sources during storms as a dominant feature of the Pulse-Shunt Concept. Consequently, current conceptual models require a runoff generation mechanism to transport DOC from its source to the stream channel.

As an alternative hypothesis, we conceptualize a system in which runoff generation and solute sources may be decoupled, with solutes generated within the stream itself and runoff generated from the riparian zone and hillslopes (hereafter the ‘channel source hypothesis’). We propose that DOC may be generated and/or stored at high concentrations in channel dead zones and can be mobilized or otherwise connected to the active stream during storm events. This hypothesis is grounded in three established concepts. First, in-channel sources are already accepted for particulate loads, including stream sediment (e.g., Vansickle & Beschta, 1983; Gomi, Moore, & Hassan, 2005) and mobilization of stored particulate organic carbon previously input to the stream from allochthonous sources (e.g., McDowell and Fisher, 1976; Vannote, Minshall, Cummins, Sedell, & Cushing, 1980; Argerich et al., 2016). Next, POC deposits in streams and streambeds are ubiquitous and serve as an in-stream source of DOC (Meyer, Wallace, & Eggert, 1998). In-channel DOC production provides a mechanism by which DOC can be produced in the channel without a corresponding inflow of water. Finally, dead zones - locations in the stream with residence times that functionally decouple them from the stream channel (Gooseff, LaNier, Haggerty, & Kokkeler, 2005; Jackson, Haggerty, Apte, Coleman, & Drost, 2012) are likely to collect and store organic matter at low flows but can be readily mobilized during storms. Taken together, these well-established mechanisms underpin the conceptual basis for the channel source hypothesis. Notably, a few studies invoke channel sources as a possible explanation for observations, but have not had sufficient field data to reject other, equally plausible mechanisms (Meyer & Tate, 1983; Buffam, Galloway, Blum, & McGlathery, 2001).

Here, we examine the channel source hypothesis as an explanation for observed DOC dynamics during a small storm in a temperate, mesic, forested catchment. We start by assessing alternative hypotheses (commonly ‘conceptual models’) that have been invoked to explain observed in-stream DOC dynamics. We use our data and results of other published studies from our study site to critically evaluate those conceptual models and show that none of those models plausibly explains our observations. An additional source of DOC is needed to explain the DOC dynamics we observed. Our data suggest that the stream channel is a plausible source for that DOC. This source has been previously overlooked by catchment hydrologists, and we suggest it should at least be considered as a potential explanation for DOC dynamics during storms and in the interpretation of concentration-discharge relationships.

2. STUDY SITE AND METHODS

The study site is located near the mouth of WS1 (Fig. 1), a 96-ha gaged watershed at the H. J. Andrews Experimental Forest in western Cascade Mountains, Oregon, USA (44.2070N, 122.2575W). The watershed is deeply incised with steep hillslopes. Occasional outcrops of more weathering resistant bedrock are present on hillslopes and along the valley bottom where the stream is constrained to bedrock chutes. Soils average about 2.0 m in depth across the basin (range <0.2 m to >5.0 m), and in most locations are underlain by deeply weathered saprolite (Jarecke, Bladon, & Wondzell, 2021). Hillslope soils are well drained and saturation does not occur within 2 m of the soil surface at any time of year (Jarecke et al., 2021). Stream channels are steep, with longitudinal gradients of ~14% in the well network reach, and the length of the network expands and contracts with changes in stream discharge. The stream network becomes spatially intermittent in summer and the length of the continuously flowing channel shrinks significantly under the driest conditions (Ward, Schmadel, & Wondzell, 2018; Ward, Wondzell, Schmadel, Herzog, 2020).

A well network was installed near the mouth of the watershed in 1997 and was composed of 6 transects of wells (Fig. 1). Transects usually had a center piezometer located in the thalweg, and three wells located on each side of the stream (see detailed descriptions in Corson-Rikert, Wondzell, Haggerty, & Santelmann, 2016). An additional hillslope well was installed in 2013, approximately 150 m upstream of the well network, just below a hillslope hollow but above a bedrock outcrop where a shallow saturated soil layer persisted year-round. Data from the WS1 catchment and well network allows us to calculate representative travel times of water through the riparian zone. Surface channels in WS1 range from 0.4 to 1.9 m wide and valleys from 2.5 to 39.2 m wide (mean 10.3 m, median 9.0m) (Ward et al., 2018). For a stream centered in the valley, hillslope runoff needs to move laterally from the hillslope to the stream an average of 4.7 m (range 1.0 to 19.4, median 4.0 m, st. dev. 2.4 m). This lateral transport would occur via saturated flow through the valley-floor colluvium. Cross-valley hydraulic gradients average about 0.05 m/m (Voltz et al., 2013) and the geometric mean of hydraulic conductivity measured in all 41 wells within the network was 7×10^{-5} m/s (Kasahara & Wondzell, 2003). Assuming a porosity 0.30 and making cross-valley estimates using Darcy's Law (Ward, Schmadel, Wondzell, Gooseff, & Singha*,* 2017) we estimate that travel from the base of a hillslope to the stream channel would take about 25 hr and 100 hr to cross the minimum and mean valley width, respectively.

We sampled the stream, the hillslope well, and 9 wells in the hyporheic and riparian zones during a storm from 15 to 17 November 2013 including pre-storm, peak flow, and recession samples (Fig. 2). For additional details on sampling and analytical protocols see Corson-Rikert (2014). This was an early wet-season storm, typical of the transition phase between dry and wet seasons (McGuire & McDonnell, 2010) during which soil moisture storage is being recharged so that hillslope contributions to storm flows are reduced compared to fully-wet antecedent conditions.

3. RESULTS

Over the 72-hour period of storm sampling, DOC concentrations were higher in the stream than in any of the other locations sampled with the exception of one sample in well G3 (Fig. 2B). Stream DOC increased early in the storm and decreased thereafter, even though discharge remained high. We observed increased DOC in the riparian and hyporheic wells, but the mean concentrations were more dilute than stream water. We also found low and constant concentrations of DOC in both the hillslope well (UHH) and well D7 which was located along the valley margin, directly below a large hillslope hollow.

Both stream water and water from well UHH had low and temporally constant concentrations of NO_3^- (Fig. 2B). The riparian and hyporheic wells were quite different, with NO_3^- increasing at the beginning of the storm and only decreasing slowly thereafter. Well D6 showed surprisingly high peak concentrations of NO_3^-, Cl^-, Mg^{2+}, and Ca^{2+} during the first peak in stream discharge (Figs. 2B, 2C). Concentrations of NO_3^- and base cations increased in well D7 late in the storm (Fig. 2B, 2C), suggesting delayed arrival of a more distal source of water that is relatively rich in solutes produced from mineral weathering reactions. Well D7, located at the base of a large hillslope hollow, most likely captures deep soil water and groundwater fracture flow from the adjacent hillslope (Pennington, 2019).

Two wells showed unexpected responses during the storm. Concentrations of DOC in well G3 increased rapidly at the onset of the storm and then decreased substantially as the storm progressed. This bankside well historically exhibits anomalous behavior during stream tracer tests, with very long travel times required for tracer to reach the well (Ward et al., 2017; Wondzell, 2006; Voltz et al., 2013) and persistently elevated concentrations of pCO_2 (Dosch, 2014). The well recovered rapidly during slug tests (Kasahara & Wondzell, 2003), however, suggesting that it was well connected to the aquifer. These characteristics might be expected from deep groundwater flowing upward into the hyporheic zone from fracture flow through the bedrock underlying the stream. However, relatively low concentrations of base cations suggest that this water is not likely to be long residence-time groundwater. Note that the high concentrations of NO_3^-, Cl^-, Mg^{2+}, and Ca^{2+} observed in one hyporheic well at the onset of the storm were from well D6, not well G3. Clearly, we cannot explain all the patterns we observe in the timing and concentrations of all solutes measured in every location within the study site. However, our data do conclusively show that no mixture of water from the sources we sampled can account for the changes in stream water chemistry we observed during the storm.

4. DISCUSSION

4.1 Critical evaluation of existing conceptual models

In this section, we present a critical evaluation of alternative conceptual models for runoff generation and solute time series. We use the data collected during the storm, information from previously published studies from this site, and our *in-situ* field observations to evaluate whether existing conceptual models are plausible explanations for the patterns we observed. If viewed from a hypothesis testing paradigm, then these conceptual models stand as null hypotheses, and the data and other observations are used to test them. If the null hypothesis is falsified, then we reject the conceptual model as a plausible explanation. If we fail to falsify or reject the hypothesis, the conceptual model remains a plausible explanation for our observations.

4.1.1 Infiltration Excess Overland Flow

The soils at WS1, like most mesic forest soils, are highly permeable (Jarecke et al., 2021) so that infiltration excess overland flow (Figure 3A; sensu Horton, 1933) is rare (Harr, 1977; McGuire & McDonnell, 2010; Amatya et al., 2016), likely only generating runoff from the few locations where bedrock outcrops to the surface and is adjacent to the stream. Because such bedrock outcrops are rare in WS1, this cannot be an important mechanism generating runoff and DOC at our site.

4.1.2 Saturation Excess Overland Flow

Lateral Saturation Excess Overland Flow.

Saturation excess overland flow (Figure 3B) is generated when the water table reaches the surface, generating overland flow composed of both groundwater and precipitation falling on the saturated areas (Dunne & Black, 1970), carrying with it a combination of the pre-event DOC in the groundwater, precipitation or throughfall DOC from the rainfall, and DOC leached from the organic and litter layers at the surface of the soil. This mechanism appears to be most common in low relief catchments (Dunne & Black, 1970; Western, Grayson, Blöschl, & Willgoose, 1999), or where soils are shallow. In contrast, hillslopes in WS1 are steep as are longitudinal valley gradients which support significant subsurface hillslope (McGuire & McDonnell, 2010) and down-valley flow (Kasahara & Wondzell, 2003; Voltz et al., 2013; Ward et al., 2018). Field observations during storms and multi-year monitoring of 11 hillslope wells located in a variety of topographic positions all confirm that saturation to the soil surface is exceedingly rare, even at the bases of large hillslope hollows near the valley floor (Jarecke et al., 2021). Taken together, the geomorphic structure of the catchment, the deep soils with high infiltration capacity underlain by relatively permeable and deeply weathered saprolite and or fractured bedrock (Gabrielli, McDonnell, & Jarvis, 2012), observations from hillslope wells, and field observations during storms all indicate that saturation excess overland flow is neither a significant source of runoff nor a viable mechanism to mobilize DOC from hillslopes to the active channel.

Channelized Saturation Excess Overland Flow

Channelized saturation excess overland flow (Gomi et al., 2005) is the mechanism by which the length of the channel network expands during storms, where convergent subsurface flows in steep headwater hollows cause the riparian water table to rise and initiate channelized flow (Ward et al., 2018; 2020). During the event we studied, discharge at the watershed outlet rose from about 7.8 to 28.5 L/s, which would expand the contiguously flowing channel from 1456 m to 1542 m, based on previous modeling of channel expansion and contraction (Ward et al., 2018). The primary source of runoff generation via this mechanism would be pre-event water stored within the riparian zone along ephemeral streams or within unchannelized hillslope hollows. Pre-event riparian and hyporheic observations show that DOC ranged from 0.2 to 1.11 mg/L, all too dilute to explain the observed in-stream peak of 3.3 mg/L. Thus, while this mechanism is hydrologically plausible, the DOC concentrations in the pre-event water are too dilute to explain observed DOC concentrations.

4.1.3 Hillslope Subsurface Stormflow Generation

At least two somewhat unique mechanisms have been proposed to explain how subsurface drainage from hillslopes can generate rapid stream flow responses during storms. Hewlett and Hibbert (1967) described a translatory-flow mechanism (Figure 3C) through which pressure generated in the saturated zone by rainwater infiltrating hillslope soils is rapidly transmitted through connected pore spaces and pushes water from the bottom of the hillslope into the stream. This mechanism allows for rapid response and is consistent with observations that rising limbs of hydrographs are dominated by "old" or "pre-event" water (Neal & Rosier, 1990; Kirchner, 2003). The translatory-flow mechanism, as initially described, assumed that unsaturated flows occurred through the soil matrix. However, DOC leached from organic-rich horizons is often adsorbed in the mineral soil (Yano, Lajtha, Sollins, & Caldwell, 2005) so that DOC concentrations are quite low in deep soil-water (McGlynn & McDonnell, 2003; van Verseveld et al., 2008). Thus, the concentrations of DOC or other solutes in "old water" may not suffice to explain changes in stream water chemistry. Further, isotopic data suggest some proportion of "new" or "event" water is present (Brown, McDonnell, Burns, & Kendall, 1999). Thus, attempts to explain the observed changes in the concentration of solutes in stream water during storms often require that some portion of the infiltrating rainfall flow rapidly from hillslopes to streams, bringing with it chemical signatures acquired in the canopy or the organic soil horizons.

Preferential flow (Figure 3D & E) allows water from various sources and chemistries to move rapidly from hillslopes to streams and can occur through macropores (Beven, 1989), even when the soil matrix is not saturated, along contacts between soils and bedrock (McDonnell, 1990) or through bedrock fractures (Figure 3F; Gabrielli et al., 2012). Further, because of limited contact with mineral surfaces of the soil matrix, preferential flows can preserve chemical signatures of the source water. Thus, throughfall, stem flow (Qualls & Haines, 1992; Hinton, Schiff, & English, 1998; Brown et al., 1999), and drainage from the soil litter and organic horizons can all be routed to the stream with "new" or "event" water signatures.

It is clear that, like most mesic forested catchments, the primary runoff generation mechanism in the H.J. Andrews Experimental Forest is subsurface stormflow (Harr, 1977; McGuire & McDonnell, 2010; Gabrielli et al., 2012). The combination of highly porous soils and highly fractured or deeply weathered bedrock, combined with steep hillslopes, drive saturated subsurface flow down hillslopes to the valley margin or directly to the stream in headwater channels lacking a floodplain (after Hewlett & Hibbert, 1967). Preferential flow paths through the mineral soil and the network of fractures in the bedrock, however, have been identified as a mechanism to route relatively DOC-rich, new (or "event") water to the stream (Gabrielli et al., 2012). Thus, runoff generated at the hillslope becomes a source of solutes to subsurface stormflow. Indeed, this mechanism has been studied in some detail at WS10 in a nearby 10-ha catchment with a highly instrumented hillslope draining into a trench; elsewhere in WS10, the hillslopes drain directly to the stream because the riparian zone was removed by a debris flow in 1986 (McGuire & McDonnell, 2010).

The subsurface flow mechanisms described above appear to be a plausible mechanism, both to generate peak flows and the DOC loads necessary to explain the patterns we observed during the storm. However, unlike WS10, the stream channel in WS1 is separated from the adjacent hillslopes by a narrow riparian zone along most of its length. The sediment of the riparian zone is saturated, with the water table in equilibrium with the height of water in the stream. Therefore, hillslope water must pass through this saturated sediment before reaching the stream.

Riparian zones can substantially alter the time scales at which hillslope water can reach streams during storms. First, our calculations for travel times across even the very narrow floodplains present in WS1 suggest that neither runoff nor DOC generated from the hillslopes can reach the stream channel quickly enough to explain changes in DOC concentrations on the rising leg of the storm hydrograph given that only 15 hr elapsed from the beginning of the storm to the observed peaks in discharge and DOC. In fact, the lateral vector of head gradients and subsurface flow velocities through the saturated colluvium of the valley floor suggest that water will flow only 0.65 m in those 15 hours. (Note, we do not see saturation of organic-rich, near-surface soil horizons in the riparian zone that could speed delivery of riparian water to the stream (Figure 3H, but see Section 4.1.5).

Not only are travel times too long for hillslope water to reach the stream in advance of the peak in discharge, but the DOC concentrations in this water are too dilute to serve as a source of DOC to the stream water. Wells at the valley margin, penetrating the full depth of the saturated zone and located immediately below hillslope hollows should capture hillslope water because both matrix flows as well as preferential flows through macropores in hillslope soils, or along the soil-bedrock interface, cannot bypass the saturated sediment of the valley floor. Well UHH is located on the lower hillslope, several meters above the valley floor and can only receive hillslope sources of water. The distinct chemistry of well D7, compared to all other riparian/hyporheic wells, suggests it receives some combination of deep soil water and longer residence-time groundwater. Both stream tracer tests (Voltz et al., 2013; Ward, Gooseff, & Singha, 2013) and damped and lagged seasonal temperature fluctuations (Pennington, 2019) suggest that this well has limited connectivity to stream water, even at baseflows. Well D7 also has relatively high concentrations of base cations indicative of bedrock weathering, and late in the storm, concentrations of base cations increase suggesting that storm flows push additional long-residence time groundwater into the floodplain margin. The observed maximum DOC concentrations in well UHH was 0.64 mg/L and was 0.32 mg/L in well D7. In contrast, stream water DOC concentrations peaked at 3.29 mg/L. Clearly, the observed concentrations of DOC in hillslope subsurface storm flows – including the shallow soil water likely captured by well UHH and the deeper soil water or groundwater captured by well D7 – cannot serve as a source for the stream DOC concentrations. Thus, both the timescales of cross-valley flows and the dilute concentrations of DOC observed in the hillslope source waters rule out the hillslopes as an explanation for the high DOC concentrations observed in the stream during the storm.

4.1.4 *Fracture flow bypassing the riparian zone*

Unlike hillslope-source soil water, fracture flow (Figure 3F) could bypass valley margin wells. Further, both flow through fractured bedrock (van Verseveld et al., 2008; Gabrielli et al., 2012) and transient groundwater (van Verseveld et al., 2008) have been identified as the dominant source of DOC during storms in the nearby WS10 catchment. Thus, groundwater upwelling from the fracture network in bedrock beneath the valley floor could be a potential source of water that could explain the DOC concentrations we observed in the stream. It seems unlikely, however, that fracture flows could bypass the entire riparian zone and our well network, and flow directly into the stream channel. Rather, if large inputs of DOC-rich groundwater from fractures in the bedrock of the valley floor were present, they should mix with other sources of water in the shallow floodplain aquifer and we should observe high DOC concentrations throughout the well network. Instead, we only observed high DOC concentrations in a single well. Thus, we see no evidence that fracture flow of shallow groundwater can be an important source of DOC.

4.1.5 Riparian Zone Subsurface Stormflow Generation

Near-stream areas, especially the riparian zone and near-stream wetlands, can be an important source of DOC to streams (e.g., Fiebig, Lock, & Neal, 1990). This DOC can be flushed to streams over a period of weeks as "variable source areas" expand during snowmelt (Hornberger, Bencala, & McKnight, 1994; Boyer, Hornberger, Bencala, & McKnight, 1997). Similarly, near stream saturated areas have been documented as an important source of both runoff and DOC to streams during storms since this mechanism was first described by Dunne and Black (1970). Alternatively, water tables in the riparian zone often rise rapidly during storms, and if they reach more organic-rich shallow soil horizons, these soils can serve as a source of DOC (Figure 3H). Further, saturated conductivity is often greater in organic rich surface horizons than deeper soil horizons, or rising water tables can activate preferential flow paths. Regardless the specific mechanism, flow through shallow, organic rich horizons can move rapidly to the stream so that the riparian zone is a source of both runoff and DOC early in the storm hydrograph (McGlynn & McDonnell, 2003; Bishop et al., 2004).

The riparian source hypothesis has been previously invoked as an explanation for the clockwise hysteresis between DOC and discharge observed in our study site (WS1) and other small catchments at the H. J. Andrews Experimental Forest (Hood, Gooseff, & Johnson, 2006). This conclusion, however, was based only on observations at the catchment outlet; supporting measurements were not made within the catchments' riparian zones. Our observations, however, reject near-stream saturated areas as a source of DOC because we do not observe surface saturation at our site. Our data also suggest that shallow preferential flows could not have occurred during the storm we monitored. The storm responses of WS1's riparian/hyporheic subsurface flow dynamics were carefully monitored during a storm in 2010 (Voltz et al., 2013) when peak discharge exceeded 1.5 mm/hr. Despite heavy rainfall and very high peak flows, the overall shape of the subsurface flow net changed very little. And the 2010 storm was much larger than the storm we monitored in November 2013 when peak discharge only reached 0.1 mm/hr. Thus, during the storm subsurface water flows through the saturated layer of colluvium for which we have calculated flow velocities (see Section 2). At the timescale of the storm, matrix flows could only contribute water and solutes to the stream from portions of the riparian zone that are $<$ 1.0 m from the channel. Clearly, there is no evidence that water in the riparian zone could be mobilized rapidly enough to contribute to observed in-channel DOC dynamics. Moreover, even if this mobilization were hydrologically plausible, DOC concentrations in this water are too dilute to explain the observed concentrations of DOC in the stream water. Our data conclusively show that the riparian zones of WS1 cannot be the source of significant runoff nor DOC to the stream early in the storm.

4.1.6 Activation of Distal Patches

Gannon et al. (2015) attributed in-channel DOC dynamics in headwaters by carefully tracing water and DOC from rapidly activated patches high in the catchment (Figure 3I). Critically, these patches had a direct, rapid mechanism to hydrologically connect to 0 and 1st order streams draining the basin. Similar patterns have been observed at the Panola Mountain Research Watershed where a rock outcrop covers 35% of the studied catchment and contributed 50% and 85% of stream discharge during the two storms studied (Burns et al., 2001). While our study catchment has outcrops of bedrock, their area is small and they are not readily connected to the surface stream network. We do not see well defined ephemeral channels below the larger outcrops, high on the hillslopes. Consequently, bedrock runoff infiltrates the soils below the outcrops, remaining subsurface as it flows through hillslope hollows, and only emerges into the stream network where channelized saturation overland flow activates a stream channel (Ward et al., 2018; 2020). While we did not sample runoff from any distal patches, the lack of a mechanism to transport any runoff generated to the outlet at the timescales observed is the basis for deeming this mechanism implausible.

4.2 Channel Source Hypothesis

We were surprised that DOC concentrations in the water samples from both the riparian and hillslope wells were lower than the stream water. We had expected that the riparian zone would have been the predominant source of DOC to the stream early in the storm hydrograph as suggested by a previous study of storm exports of DOC from WS1 (Hood, Gooseff, & Johnson, 2005). This unexpected observation forced us to consider other explanations for the patterns we observed in the stream chemistry. However, as we detailed above, none of the widely accepted conceptual models appear to provide a plausible explanation when critically examined against our observations and other studies within the catchment, forcing us to consider an alternative or "missing" source for the DOC.

Treating the channel as a source for DOC (Figure 3J) in WS1 appears plausible based on seasonal patterns in both litter fall and stream DOC concentrations as well as the amount of organic matter stored on and in the streambed. Tree cover in the WS1 riparian zone is dominated by red alder, an early-successional deciduous tree that colonized the riparian zone after logging. Leaf fall occurs from October through November. Litterfall studies in WS1 suggest that 160 g/m^2 of the dry season litterfall (Frady, Johnson, & Li, 2007) could be stored in the channel at the time of our storm event after accounting for rapid leaching losses of 30% of the mass of freshly fallen leaf litter. Given an approximate channel area of 1550 m^2, the channel could store as much as 250 kg of recently fallen leaves. If 100% of the increased DOC over pre-event concentrations were due to in-channel sources, the stored DOC would have had to supply some 4.45 kg carbon during the storm we monitored. Assuming 40% of the mass of organic matter is carbon (stoichiometry based on CH_2O), the DOC load associated with the storm would represent 11.1 kg of organic matter, or 4.5% of the direct litterfall accumulated during and after one growing season. Importantly, our estimate above is conservative. Frady et al. (2007) did not measure litter inputs during November so our flux calculations do not include any litter inputs for the first two weeks of November when alders would still be losing their leaves. Also, our estimates only consider the current growing season's leaf litter and neglect longer-term storage of fine- and coarse-particulate organic matter. Organic matter budgets for the nearby WS10 suggest that standing stocks of particulate OM < 10 cm in diameter typically range between 700 and 800 g C m^{-2} in 1^{st}- and 2^{nd}-order streams (Cummins et al., 1983). Their data suggest that the channel network in WS1 would store between 1,000 and 1,200 kg of C; exports from this single storm would equal ~0.4% of that carbon. Finally, our flux estimates do not include the potential for large in-stream wood to contribute DOC during the storm. In WS10, solubilization of only 0.1% of the large in-stream wood would account for the entire annual DOC flux from that stream (Sedell, Triska, Hall, Anderson, & Lyford, 1974). Clearly, the export of DOC during the November storm was small, given these estimates of annual litter fall inputs and OM storage, supporting the idea that the channel is a plausible source for this DOC.

4.3 Catchment Hydrologists' and Aquatic Ecologists' Conceptual Models

We, like other catchment hydrologists, did not start out considering the channel as a potential source for solutes in stream water during storms. In some ways, this is surprising. As catchment hydrologists, we already accept the channel as the source of suspended sediment, including particulate organic carbon (POC). Suspended sediment often shows concentration responses similar to DOC – with concentrations increasing rapidly on the rising leg of the hydrograph, a clockwise hysteresis, and a flushing response of in-channel storage between successive storms (e.g., Vansickle & Beschta, 1983). Further, the distinction between particulate and dissolved is operationally determined by retention or passage through a filter, but the choice of filter was determined by the smallest pore size that could be reliably manufactured and was available in early studies, resulting in an arbitrarily defined pore size of 0.45 µm (Ward and Harr, 1990). However, there is little reason to think that there would be significant difference in the properties of organic matter that was 0.046 µm versus 0.044 µm in diameter. Yet, this arbitrary size threshold marks a paradigm gap in our commonly accepted conceptual models. Particles are eroded, usually from the channel bed and banks but also from surface soils if overland flow occurs. Solutes are sourced with, and transported with, the water and therefore cannot be "eroded" from the channel.

Stream ecologists have long studied carbon cycling, although primarily during baseflow periods (Butturini et al., 2016). Stream ecosystem processes are complex so that streams can both produce, retain and respire DOC (Hotchkiss & Hall, 2015). Water residence times (or flow velocities) are a primary control on DOC processing, with retention dominating at low flows, but as flows increase, the channel increasingly functions as a passive conduit transporting DOC through the stream network (Butturini et al., 2016; Casas-Ruiz et al., 2017) – the "pulse" in the Pulse-Shunt Concept (Raymond, Saiers, & Sobczak, 2016). It is difficult to separate allochthonous and autochthonous sources and similarly difficult to separate the effect of allochthonous OM previously stored in the channel from new inputs. However, a 3-year litter exclusion study in a headwater stream in a deciduous-forest catchment in the eastern USA suggested that about 30% of total annual DOC exports were likely sourced from the channel

(Meyer et al., 1998). Further, they noted that in-channel DOC sources were bigger in the fall and winter than in the spring and summer and bigger during periods of increasing stream discharge than during baseflow periods. Perhaps not surprisingly then, stream ecologists have previously suggested that a channel source could explain the rapid response observed for DOC during storms (Meyer & Tate, 1983; Buffam et al., 2001).

Here, we focus on the rapid responses in DOC observed during storms and, following the insights of Meyer & Tate (1983), Meyer et al. (1998) and Buffam et al. (2001), suggest that organic matter stored in the bottoms of pools, channel edges, secondary channels, and in the ephemeral portions of the upper extent of the channel network can serve as a source for the pulses of DOC observed during storms and can explain clockwise patterns of hysteresis. We hypothesize that the layered structure of OM mats combined with the paucity of advective flow through dead zones would allow DOC to accumulate within the stored organic matter. This DOC would be released into the stream water as increasing discharge scoured OM from the streambed. The channel source hypothesis (Figure 3J) is unique among the conceptual models of runoff generation because it decouples the solute source from runoff generation. This decoupling is at odds with most previously published conceptual models and adds a dimension that should be considered amongst possible explanations for observations of hysteresis at catchment outlets. While we do not presently know the importance of this mechanism across all networks, the fact that it relies only upon the presence of a stream responding to a storm, which is itself a necessary condition for hydrologic interpretations of in-stream dynamics, suggests it could be ubiquitous.

We suggest that the channel is likely to be a source of DOC in temperate forested headwater streams during and after autumnal leaf fall. At that time of year, stores of recently deposited particulate organic matter should be large relative to the size of the stream, week- to multi-week-long intervals between storms will provide time for DOC to accumulate in the deposits, after which occasional storm events physically disturb the POC and mobilize the DOC stored within. Further, we expect channel sources of DOC to respond much like channel sources of suspended sediment that show seasonal depletion (VanSickle and Beschta, 1983). A storm will deplete DOC stored in the channel so that a subsequent storm will need to be larger to show the same DOC response or a substantial period of time will be needed for new DOC to accumulate. Further, as DOC is lost through a sequence of storms throughout the fall and winter, and under colder winter stream temperatures, the remaining carbon in the organic matter deposits will be less readily mobilized. Consequently, channel sources of DOC will be much reduced by late winter and spring. The storms that mobilize DOC do not necessarily need to be large, especially the first storms after leaf fall, they only need to be large enough to mobilize deposited organic matter. We also expect that intermittent streams may be 'hot spots' for the accumulation of DOC, for example in disconnected pools or locations where beds remain wet but not flowing. Further, intermittent streams constitute significant lengths of the headwater portions of river networks. In contrast to temperate, forested, headwater streams, we would not expect channel sources of DOC to be important in larger streams and rivers where litter inputs are less important (Vannote, Minshall, Cummins, Sedell, & Cushing, 1980), or in streams without distinct seasonal peaks in litter inputs. Nor would we expect channel sources of DOC to be equally important throughout the year.

5. CONCLUSIONS

Stream channels can store, transform, and release substantial amounts of organic matter. Because the standing stocks of POC are quite large in headwater streams of the Pacific Northwest, it would seem reasonable to expect that in-channel POC could also be an important source of DOC in these streams. However, this mechanism has not been systematically studied as a DOC source by catchment hydrologists in comparison to terrestrial sources. Catchment hydrologists have traditionally used stream water DOC as a basis for inferring runoff generation mechanisms from the landscape, requiring that sources of water and DOC are coupled. Further, direct precipitation on streams has long been recognized as a minor contribution to storm flow. Thus, these conceptual models require that DOC must be generated in the catchment and transported into the stream channel along with runoff. In contrast, stream ecologists take DOC as part of the aquatic carbon cycle; DOC is part of a continuum of size fractions that is not necessarily associated with an inflow of water. As a consequence of these different perspectives on DOC, it is perhaps unsurprising that conceptual models of DOC sources are not perfectly aligned. In this study, we elevate the visibility of long-studied in-channel production of DOC as a source that should be considered in future studies of DOC hysteresis and when using DOC - or other solutes potentially generated in the stream channel - as hydrological tracers.

This study does not conclude that one mechanism is predominant in comparison to others in the basin. Instead, we posit that any or all of the mechanisms detailed above may be working in concert to explain observed in-channel dynamics. Critically, the evidence of in-channel hysteresis in DOC at a study site is potentially explainable by a host of different mechanisms (Fig. 3), meaning any mechanistic attribution must be based on characterization of runoff generation mechanisms and source waters within a basin. Put plainly, the shape of the concentration-discharge relationship, alone, is not a sufficient basis for inference of watershed processes. Measurements internal to catchments are required to falsify a body of potential explanations (i.e., rejecting one conceptual model over another). Based on the evidence at our field site, we contend that studies of runoff generation and/or solute dynamics should explicitly consider two additional factors. First, the channel itself may serve as a source of dissolved mass independently of any runoff generation. Second, the presence of a riparian zone and the requirement of lateral transport from hillslopes to streams may rule out several potential and previously published mechanisms when critically evaluated.

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DATA AVAILABILITY

All data included in this study are available in the H.J. Andrews Data Catalog, including stream flow (Johnson et al., 2020), meteorology (Daly & McKee, 2019), and water chemistry collected during the storm (Wondzell & Corson-Rikert, 2016).

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FIGURE LEGENDS

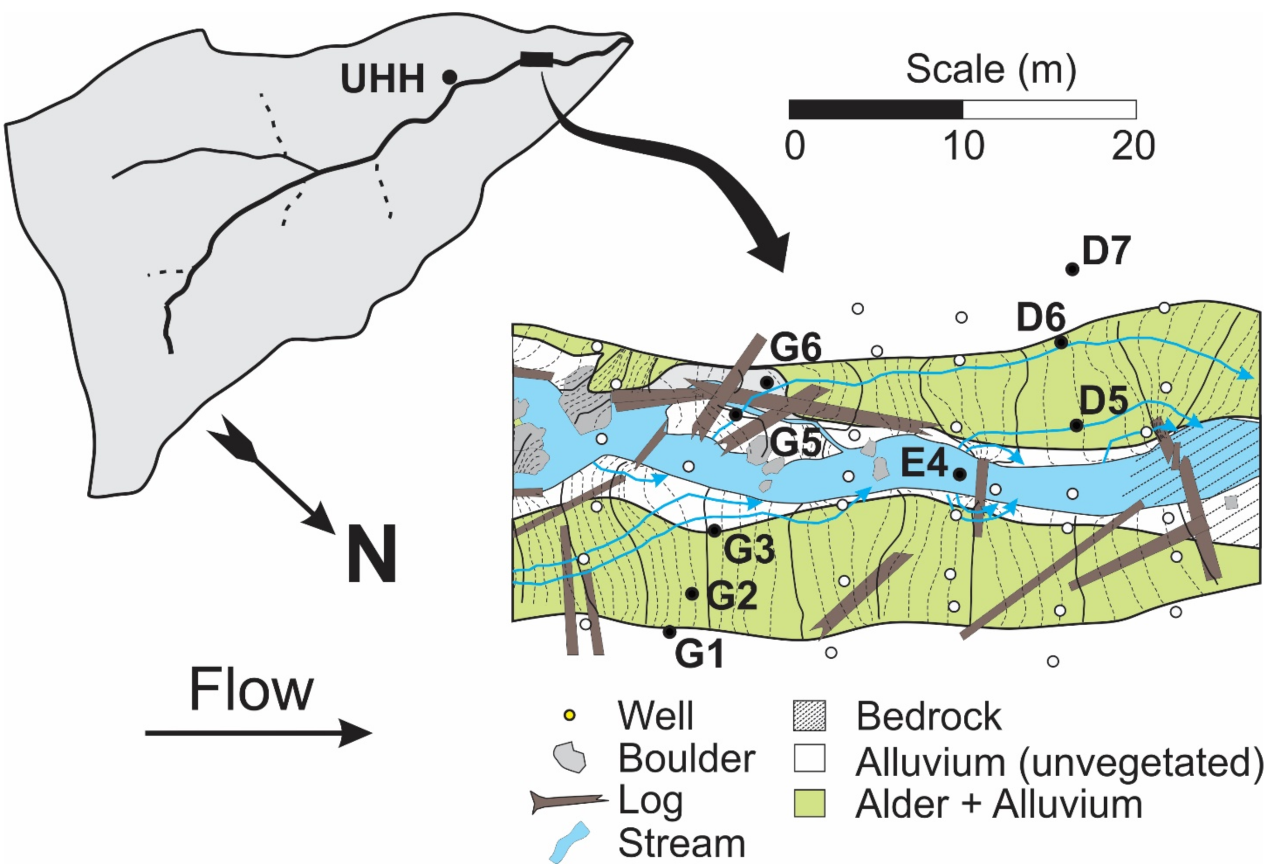


Figure 1: (A) Location of the well network (black rectangle) within the 96-ha Watershed 1 and the location of the hillslope well (UHH) upstream of the well network. Both the mainstem and primary tributary (solid lines) are spatially intermittent in summer; dashed lines indicate ephemeral tributaries. Perennial surface flow is maintained throughout the well network reach in most summers. (B) Close-up detail of the valley floor of Watershed 1 and the location of individual wells. Wells sampled during the storm are filled circles labeled “D5, etc.”. Note that maps are rotated so that flow through the well network reach is from left to right.

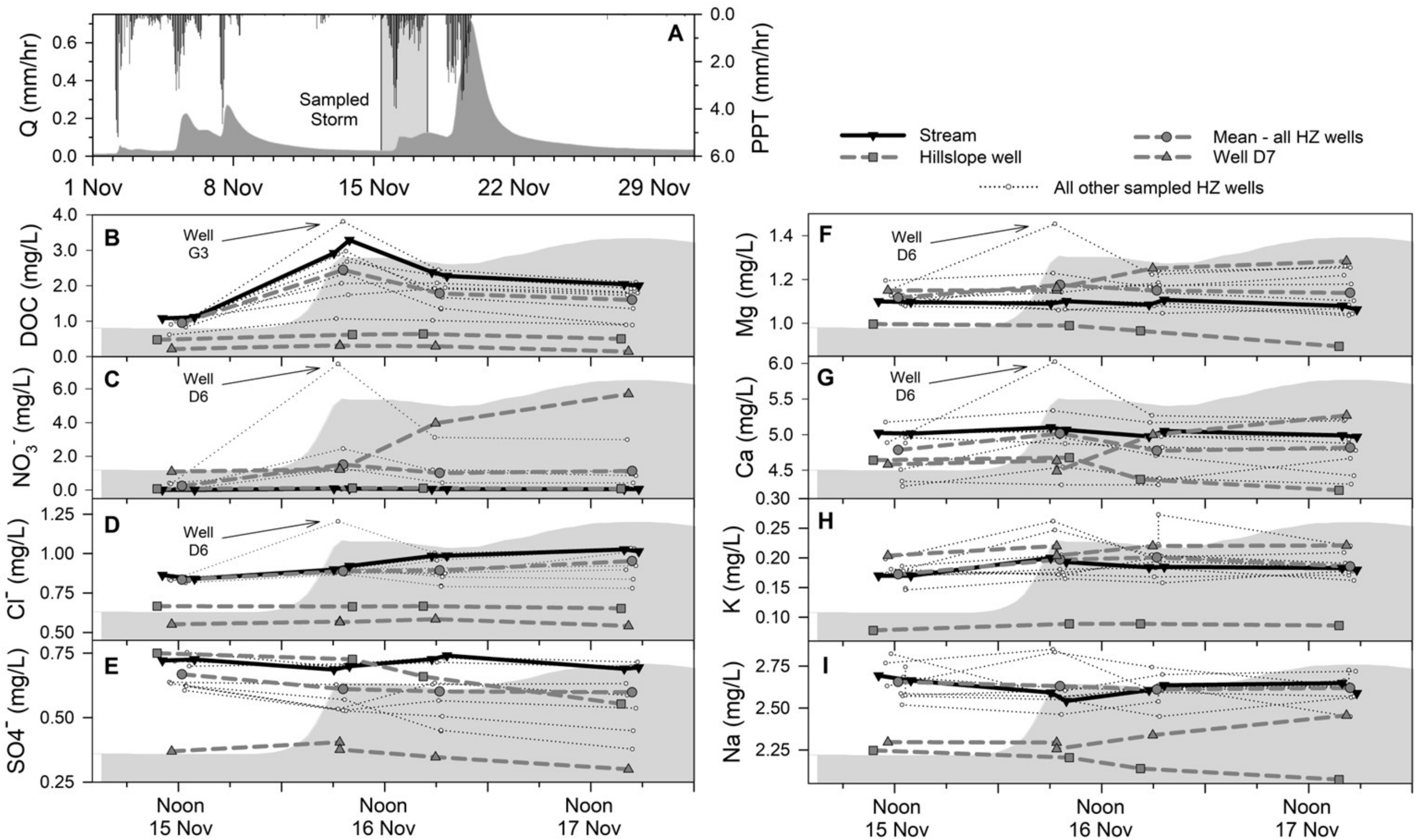
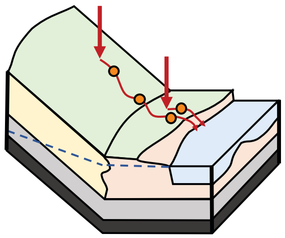
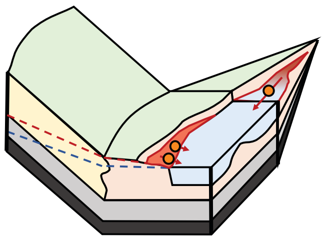
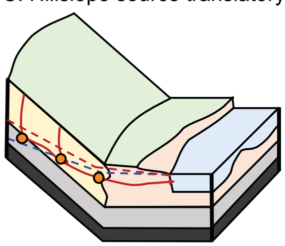
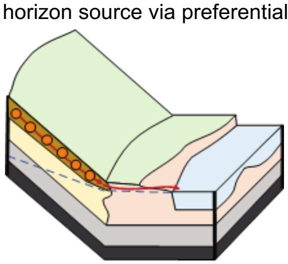
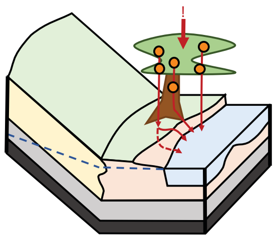
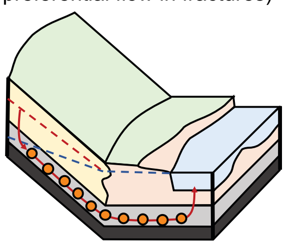
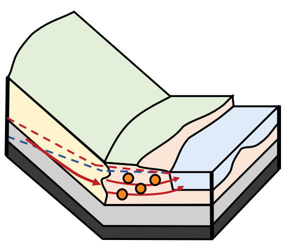


Figure 2: (A) Hourly precipitation from PRIMET benchmark station (black bars; Daly & McKee, 2019)) and hourly mean discharge recorded at the WS1 gage (dark gray shading; Johnson, Rothacher, & Wondzell, 2020). Shaded rectangle, spanning 15 to 17 November indicates the storm during which samples were collected. (B-I) Solute concentrations measured in the stream and the well network during the storm (Wondzell & Corson-Rikert, 2016).

Conceptual Model & Literature	Hydrological Requirements	DOC Requirements	Key Literature
A. Hortonian overland flow and DOC 	Infiltration excess overland flow generation *Evidence: Flow generation mechanism never observed nor reported at our study site.*	DOC source along land surface mobilized by runoff *Evidence: Not measured.*	(Horton, 1933)
B. Dunne overland flow 	Saturation excess overland flow generation in lateral or longitudinal dimension *Evidence. No lateral expansion observed. Longitudinal expansion of channel network expected from prior modeling.*	High DOC source in (a) the water that rises to intersect the land surface and/or (b) precipitation *Evidence: Pre-event DOC in riparian waters too low to explain DOC concentrations in-stream.*	(Dunne and Black, 1970; Schiff *et al.*, 1997)
C. Hillslope source translatory flow 	Piston flow (or translatory flow) from hillslopes to valley bottom *Evidence: Expected based on studies in nearby hillslopes and dominant runoff generation mechanism in our basin. However, timescales across riparian zone limit contributions to rapid DOC response in the stream.*	Low DOC in subsurface runoff from hillslopes due to adsorption in mineral soil *Evidence: DOC observed in translatory flow (wells UHH & D7) too low to explain DOC concentrations in stream water at peak storm flow.*	(McGlynn and McDonnell, 2003)
D. Hillslope source translatory flow (O-horizon source via preferential flow) 	Rapid flow through highly permeable, transiently saturated shallow, organic-rich soil horizons in near-stream zones *Evidence: Shallow water tables not observed on hillslopes; change in water table elevation in riparian zone is small. Transport across riparian zone too slow to contribute to rising limb of DOC.*	High DOC source in the water is near-surface soil horizons *Evidence: DOC observed in translatory flow (wells UHH & D7) too low to explain DOC concentrations in stream water at peak storm flow. DOC in riparian wells does not rise fast enough to connect hillslope to stream.*	(Bishop *et al.*, 1990; McGlynn *et al.*, 1999)

E. Hillslope source translatory flow (throughfall source via preferential flow) 	Preferential flow of throughfall or stemflow through soil macropores or along soil-bedrock contact from hillslope to stream *Evidence: Mechanism cited in nearby WS10. Transport across riparian zone too slow to contribute to rising limb of DOC.*	Various event-water DOC signatures from through fall or soil organic horizons preserved enroute to stream. *Evidence: High DOC concentrations not observed in wells UHH & D7.*	(McDonnell, 1990; Verseveld *et al.*, 2008; Gabrielli *et al.*, 2012)
F. Hillslope source translatory flow (via preferential flow in fractures) 	Preferential flow through fractures in saprolite or bedrock from hillslope can bypass saturated valley-floor sediment enroute to stream. *Evidence: Likely - WS10 studies, but must expect upwelling across/along whole valley floor so riparian mixing & transport makes it too slow to reach stream*	Various event-water DOC signatures from throughfall or soil organic horizons preserved enroute to stream. *Evidence: High DOC concentrations not observed in any hyporheic or floodplain wells. No observation of base cation changes in stream that would be expected with this mechanism.*	(Gabrielli *et al.*, 2012)
G. Translatory flow displaced riparian water 	Translatory flow from hillslopes displaced pre-event water in riparian zone *Evidence: Minimal response of riparian wells to larger storm events [Voltz et al., 2013] suggests no discernable pressure wave is generated.*	High pre-event DOC concentrations in riparian zone *Evidence: Pre-event riparian samples do not have sufficiently high DOC to explain in-stream observations.*	(McGlynn and McDonnell, 2003)

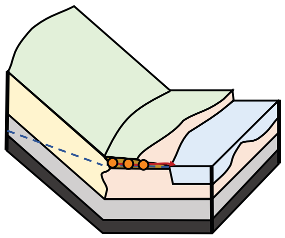
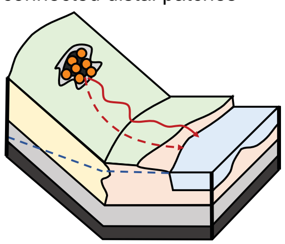
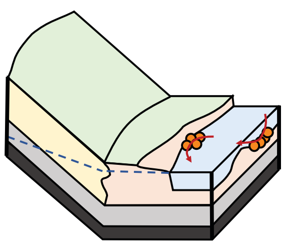
H. O-Horizon DOC from riparian zone 	Preferential flow laterally from riparian zone to stream *Evidence: No mechanism to connect source water to stream at relevant timescales for observed hysteresis.*	High DOC in shallow subsurface preferential flow Evidence: *Not observed in hyporheic nor riparian wells*	(Schiff *et al.*, 1997)
I. Mobilization of DOC from rapidly connected distal patches 	Runoff generation from bedrock outcrops and locations with shallow soils rapidly connected to stream *Evidence: No mechanism to connect source water to stream at relevant timescales for observed hysteresis.*	High DOC in runoff from distal patches *Evidence: Not measured*	(Burns *et al.*, 2001; Gannon *et al.*, 2015; Zimmer and McGlynn, 2017)
J. Channel source 	Hydrological response generates high flow in stream channel *Evidence: observed in-channel hydrograph regardless of runoff generation mechanism(s)*	Mobilization of DOC from in-channel leaf packs *Evidence: Large store of in-channel leaf litter, seasonally high DOC at start of rainy season.*	(Meyer and Tate, 1983; Meyer *et al.*, 1998; Buffam *et al.*, 2001) & this study

Figure 3. Alternative conceptual models that have been used to explain in-stream DOC hysteresis. Each model includes a summary of the evidence that would need to be observed to support the conceptualization, the evidence we found (italics), and key papers invoking or describing the conceptual model.