Variation of dissolved organic carbon during snowmelt in soil and stream waters of two headwater catchments, Summit County, Colorado

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Abstract Hydrological controls on the spatial and temporal variation of dissolved organic carbon (DOC) were investigated in the Deer Creek and Snake River catchments, located in the Rocky Mountains near Montezuma, Colorado. Measurements at these sites during spring snowmelt showed that stream DOC concentrations increased with the rising limb of the hydrograph, peaked before maximum discharges, then declined rapidly as melting continued. Hydrological catchment responses, including flow paths through and residence times of water in the catchment, are among the main factors controlling DOC variation in such headwater streams. Our objectives were to document aspects of the spatial variation of landscape DOC source areas and to determine quantitative characteristics of the flushing response. At a variety of locations within the basins, DOC concentrations were measured in the vadose zone, in the saturated zone, and in the streams. Water sampled from lysimeters in the upper soil showed an accumulation of DOC during periods of low flow and a pronounced decline in DOC concentration during snowmelt. Results indicated that spatial and temporal variations of snowmelt and soil properties, in addition to topography, are important determinants of the catchment hydrochemical response.

INTRODUCTION

Processes controlling dissolved organic carbon (DOC) dynamics continue to be a topic of interest relevant to stream ecosystems. DOC is an important component of the carbon cycle and energy balance in streams, interacts strongly with other dissolved substances (heavy metals in particular), and plays an important role in contaminant transport.

Several studies in upland catchments of the Colorado Rocky Mountains show that stream DOC concentrations rise during snowmelt on the ascending limb of the hydrograph, peak prior to maximum discharge, then decrease rapidly as melt continues (Lewis & Grant, 1979; McKnight & Bencala, 1990; Denning *et al.*, 1991; Hornberger *et al.*, 1994). Hydrological catchment responses, including flow paths through and residence times of water in the catchment, are among the main factors controlling DOC variation in such headwater streams. The temporal variation of DOC in stream water can qualitatively be attributed to flushing of a soil DOC pool by infiltrating melt water (Lewis & Grant, 1979; Baron *et al.* 1991; Hornberger *et al.*, 1994). Conceptually this suggests that soluble organic carbon accumulates in the upper soils of the catchment, when subsurface flow is predominantly through the lower soil horizons, due to such processes as microbial degradation of annual litter (from grasses and willows) and of soil organic matter (McKnight *et al.*, 1993). During snowmelt, the water table rises and creates increased flows toward the streams through the upper soil horizon, flushing the DOC enriched soil waters to the stream channels (Hornberger *et al.*, 1994). Flushing of DOC from soils into stream water has been documented in response to both rain and snowmelt in areas outside of the Rocky Mountains as well (Foster & Grieve, 1982; Meyer & Tate, 1983; McDowell & Likens, 1988).

Patterns observed in stream water of the Deer Creek and Snake River basins near Montezuma, Colorado, exhibit such a characteristic flushing response during snowmelt. In this paper, we investigate catchment inputs of DOC to these streams. Our working hypothesis is that soils of the catchment are the primary source of DOC to streamflow. Our objectives are to document aspects of the spatial variation of landscape DOC source areas and to determine quantitative characteristics of the flushing response.

SITE DESCRIPTION

We present data from the Snake River/Deer Creek catchment, located in the Rocky Mountains of Summit County, Colorado near Montezuma (Fig. 1). A detailed description of the basin is provided by Theobald *et al.* (1963). The headwater basin ranges in elevation from about 3300 to 4210 m, and is bounded by the Continental Divide to the south and east. Snake River and Deer Creek, neighboring subcatchments, are divided by Teller Mountain and drain areas of 12.0 km^2 and 10.6 km^2, respectively. The Snake River and Deer Creek stream channels merge together at a confluence just south of the town of Montezuma (Theobald *et al.*, 1963).

Snake River and Deer Creek are similar in terms of their vegetation and appearance. About half of the catchment is above the treeline. Throughout most of the catchment willow and birch bushes fringe the riparian zone, while sedges predominate on the slopes between the stream channels and an upland pine and spruce forest. In the lower third of the catchment, the valleys narrow and stream gradient is steeper. Here the forest, composed mainly of *Abies lasiocarpa, Pinus contorta,* and *Picea engelmannii*, extends to the stream banks.

The Snake River valley is underlain predominantly by granitic rocks of the Idaho Springs Formation (Theobald *et al.*, 1963). The upper part of this valley is covered by a bog iron ore deposit. Zones of the host rock contain large amounts of disseminated pyrite; thus extensive pyrite weathering gives rise to acidic, sulfate-rich soil interstitial and stream water (Theobald *et al.*, 1963). In contrast, the Deer Creek catchment is chiefly underlain by Swandyke Hornblende Gneiss (Theobald *et al.*, 1963) and is generally pristine (Bencala *et al.*, 1987). Although sulfide rich veins dot the landscape and have been mined extensively in the past, the water chemistry of Deer Creek has not been significantly affected (Bencala *et al.*, 1987).

KEY

*	Stream gaging stations
A	Soil water sampling sites A-H (see below)

Snake River (SN)

Site	Instrument Description	Notation
E	riparian lysimeter	SN-erl
E	hillslope lysimeter	SN-ehl
F	riparian lysimeter	SN-frl
F	hillslope lysimeter	SN-fhl
G	riparian lysimeter	SN-grl
G	hillslope lysimeter	SN-ghl
H	riparian lysimeter	SN-hrl
H	hillslope lysimeter	SN-hhl

Deer Creek (DC)

Site	Instrument Description	Notation
A	riparian lysimeter	DC-arl
A	hillslope lysimeter	DC-ahl
A	hillslope well	DC-ahw
B	riparian lysimeter, deep	DC-brld
B	riparian lysimeter, shallow	DC-brls
B	riparian well	DC-brw
B	hillslope lysimeter, deep	DC-bhld
B	hillslope lysimeter, shallow	DC-bhls
B	hillslope well	DC-bhw
C	riparian lysimeter	DC-crl
C	hillslope lysimeter	DC-chl
D	riparian lysimeter	DC-drl
D	hillslope lysimeter	DC-dhl

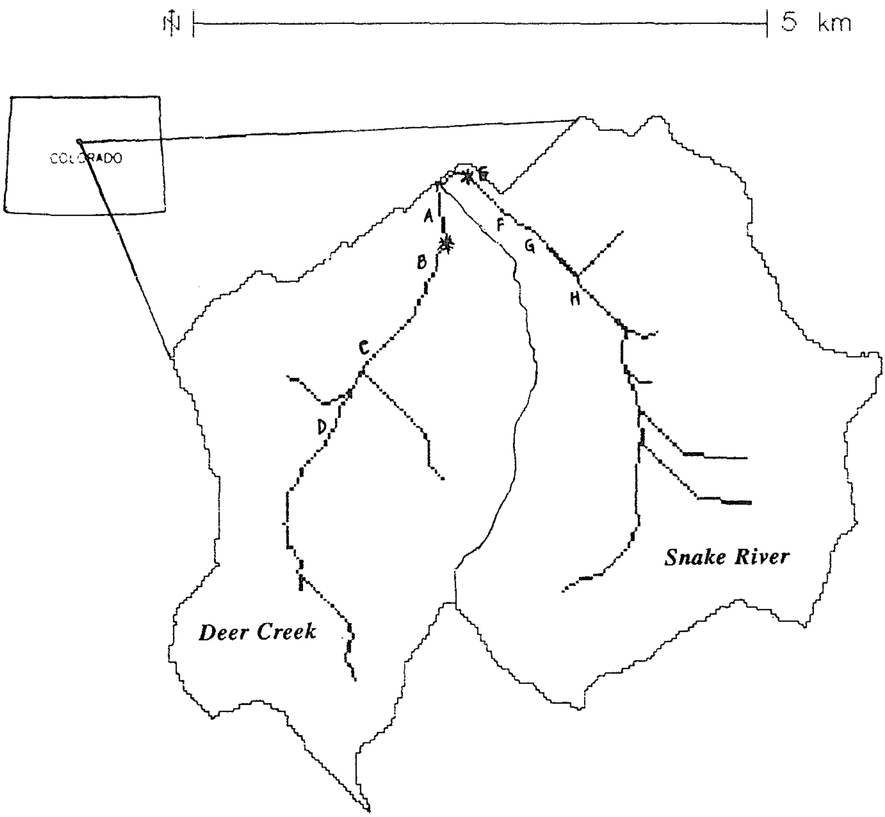

Fig. 1 Location and instrumentation of the Snake River and Deer Creek basins.

INSTRUMENTATION AND ANALYTICAL METHODS

Stream stage recorders, soil lysimeters, and wells were set up in the catchment in July 1991 (see Fig. 1). A stream gauge system was installed at the outlet of both Snake River and Deer Creek, each consisting of a bubbler gas-purge assembly connected to a pressure sensor system. Eighteen tension lysimeters were installed to provide water samples from the vadose zone, and three shallow wells were constructed in the saturated zone to provide groundwater samples.

Instrumentation was placed at four main sampling sites within each basin, chosen to be accessible and to be representative of the dominant vegetation and soil classes. At each of the site locations (A-H) a lysimeter transect was installed, including one in the near-stream riparian zone (denoted as riparian lysimeter, rl) and one somewhat farther upslope (denoted hillslope lysimeter, hl). At site B, depth stratified pairs of lysimeters were placed at both the riparian and hillslope locations, with lysimeters in both the O/A and B horizons. Riparian lysimeters were placed approximately 1 to 2 m from the stream, in areas that were mostly flat with shallow soils. Hillslope lysimeters were placed where a clear slope break was evident from that of the riparian zone, approximately 10 m from the stream. One well was installed on a hillslope at site A, amid the willow and birch vegetation species that generally fringe the streams. Two wells were installed in a forested area farther upstream at site B, in a riparian zone/hillslope transect.

Hydrological and chemical responses of the catchments were investigated between July 1991 and August 1992. Stream stage, discharge, and the level of the water table within the groundwater wells were monitored. The stream gauge record was converted to hourly discharge based on a rating curve established for this site. Water levels in the wells were measured by inserting a graduated rod, rigged for sensing a change in electrical resistance when water is contacted, and recording the depth from the ground surface to water.

DOC concentrations were measured during the snowmelt period (April through August 1992) in samples obtained from the stream, snowpack, upper soil lysimeters, and groundwater wells. Stream water was collected just downstream of the gauge. The snow samples were collected in plastic bags previously rinsed with distilled water; this snow was melted and subsequently transferred to glass sampling bottles. Samples from the lysimeters and groundwater wells were obtained by pumping the water through a draw tube. All water samples were collected in precombusted, amber-colored, glass bottles that had Teflon-lined caps. At the laboratory, samples were filtered through precombusted Whatman* GF/F glass fiber filters using a Deltaware glass filtration unit, acidified with phosphoric acid, and stored at 4°C until analysis. DOC concentrations were determined using an Oceanography International (OI) total organic carbon analyzer. (*Use of brand names is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.)

RESULTS AND DISCUSSION

Patterns of discharge and DOC in stream water

The hydrograph rose dramatically during spring melt, dominated by melting of the snowpack beginning in late April (Fig. 2). Maximum streamflow occurred in late May with peak discharges of 0.97 and 0.98 $m^3 s^{-1}$ for Deer Creek and Snake River, respectively. As snowmelt ends, the hydrographs are characterized by a steeply receding limb to baseflow conditions. DOC concentrations in Deer Creek remained steady around

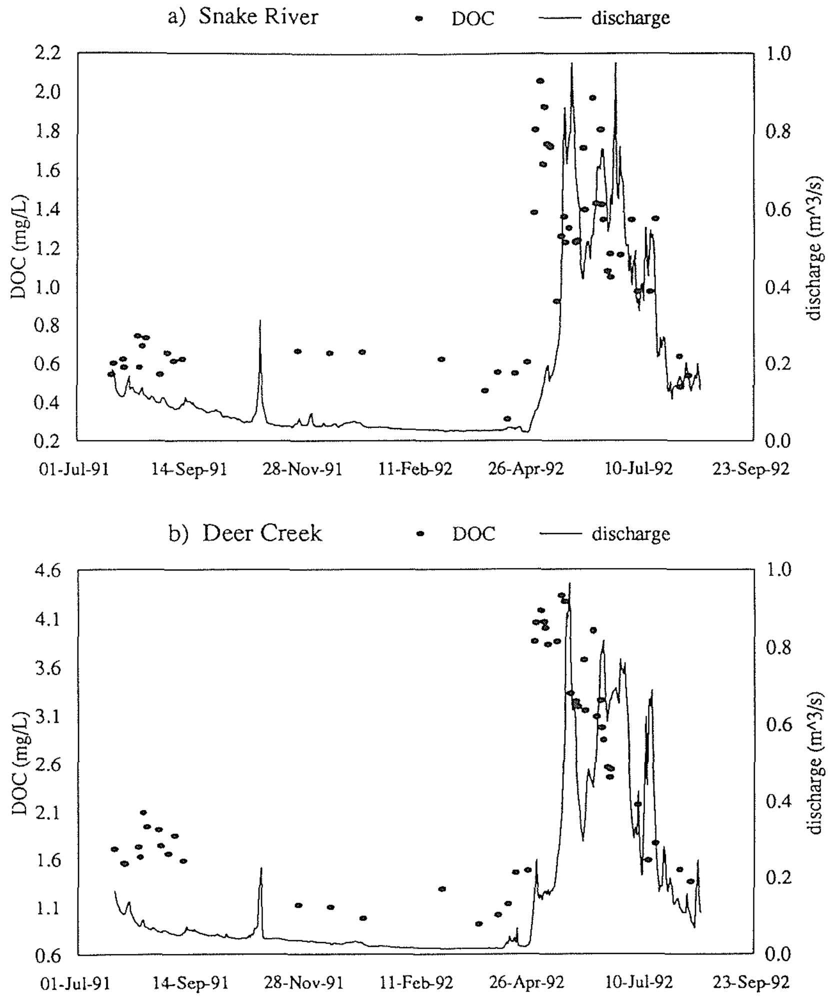

Fig. 2 Variation of DOC and discharge in stream water: a) Snake River, b) Deer Creek.

1.1 mg l^{-1} during baseflow, then increased rapidly early in the snowmelt event to peak concentrations of approximately 4.0 mg l^{-1}. In general, DOC remained significantly lower in Snake River than in Deer Creek, with concentrations that ranged from approximately 0.7 mg l^{-1} during low flow to 2.1 mg l^{-1} during snowmelt. In both catchments DOC concentrations increase rapidly just after spring melt commences, peak before peaks in streamflow, then decline continuously and rapidly as snowmelt proceeds. Such behavior is consistent with a flushing mechanism and suggests that DOC is transported from terrestrial origins.

Patterns of DOC observed in the upper soil

DOC variation in interstitial waters of the upper 0.4 m soil was observed in samples from the tension lysimeters located along Deer Creek and Snake River. Temporal

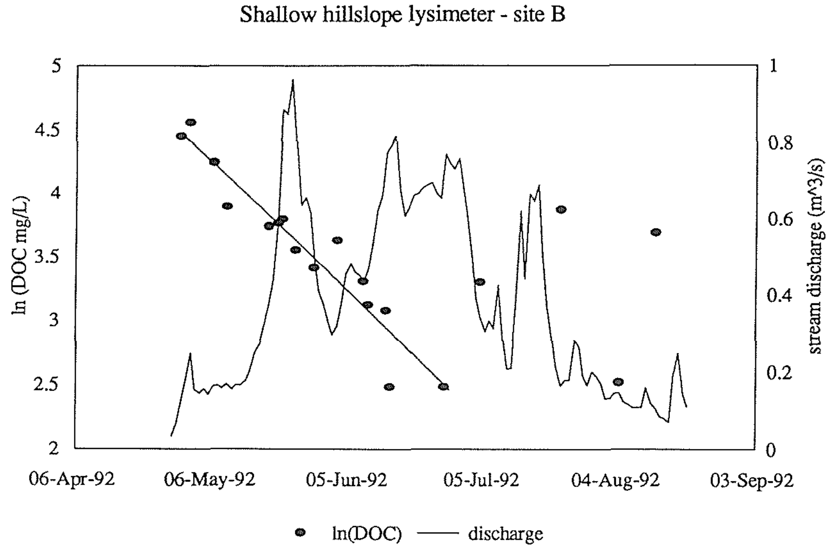

Fig. 3 Temporal variation of DOC in the upper soil (example from site B, shallow hillslope lysimeter located along Deer Creek). The straight line describes the exponential recession of DOC and represents the DOC flushing that is initiated on the rising limb of the hydrograph.

patterns of DOC in the water samples from all lysimeters showed a decrease in DOC concentrations during spring snow melt, consistent with the supposition that hydrological flushing of the upper soil during spring melt transports DOC from soil pore waters of the catchment (e.g. Fig. 3).

Landscape heterogeneities were evident in the data; the magnitude and range of concentrations observed varied substantially from site to site. In addition to the diversity of responses observed among sites, there was significant variability observed within a site, as evidenced by data collected from the depth-stratified lysimeter pairs at site B. The hillslope lysimeters are located farther upslope than riparian lysimeters but are still relatively close to the stream (approximately 10 m). Thus the degree of variation in magnitude of DOC concentrations in soils largely upslope in the catchment remains unknown.

To summarize the various patterns observed, descriptive statistics were computed for the temporal set of data collected from each lysimeter (Table 1). Samples from site SN-hrl were unusually high in DOC in comparison with all other sites, perhaps attributed to decaying roots in the vicinity of this forested sampling location. The majority of the lowest ranges were observed in riparian lysimeters. This suggests that the near-stream riparian soils may be flushed of DOC more frequently than soils located slightly upslope, as they tend to collect more subsurface water and to be more conductive.

The general pattern observed in the lysimeter samples suggests that DOC concentrations are high in upper soil interstitial waters at the end of the winter season, then are reduced as DOC is flushed during snowmelt. Looking at a semilog graph of the natural log of DOC versus time observed at each site, there is a period over the time series where DOC concentrations fall consistently from relatively high to low values. These periods were taken to represent the predominant time of flushing, and the sequential data points describing the DOC recession were used to fit a least-squares line

Table 1 Descriptive statistics of lysimeter samples (DOC in mg l^{-1}).

	Range DOC	Minimum DOC	Median DOC	Maximum DOC	No. obs.
Deer Creek site					
DC-arl	9.03	3.70	8.01	12.73	29
DC-ahl	22.88	12.14	23.95	35.02	30
DC-bhls	83.60	11.93	38.70	95.53	20
DC-bhld	51.08	4.87	34.46	55.95	21
DC-brls	41.05	3.93	8.76	44.98	18
DC-brld	77.75	4.30	16.15	82.05	14
DC-crl	0.05	3.89	7.41	12.94	14
DC-chl	35.29	7.67	17.73	42.96	17
DC-drl	8.85	9.46	14.38	18.31	3
DC-dhl	50.93	9.72	30.31	60.65	16
Snake River site					
SN-erl	73.31	6.88	30.41	80.19	21
SN-ehl	33.51	6.05	14.05	39.56	32
SN-frl	44.85	8.78	22.78	53.63	9
SN-fhl	40.15	4.43	27.44	44.58	9
SN-grl	8.93	5.34	7.04	14.27	10
SN-ghl	7.08	6.50	8.82	13.58	10
SN-hrl	153.27	17.44	63.37	170.71	12
SN-hhl	50.28	5.26	19.27	55.54	9

using linear regression (e.g. see Fig. 3). The characteristics of each line are summarized in Table 2. The number of data points used in the regression varied from instrument to instrument, ranging from 3 to 15. Although fitting a regression line for periods where just a few data points were available is prone to produce parameters with large standard errors, using this method provides a means of comparing rate responses observed among sites. Recognizing that imposing a log-linear model to describe the dominant flushing trend was better suited for data from some sites than others, the confidence in using such

Table 2 Summary of lines describing flush of DOC in upper soil.

Lysimeter site	No. of points for regression	Method rating	Slope (1/time)	Time (days) constant	Rate of flush
DC-ahl	5	fair	0.030	33.875	slow
DC-arl	6	good	0.048	20.725	medium
DC-bhld	12	fair	0.031	31.941	slow
DC-bhls	14	good	0.034	29.445	slow
DC-brld	7	fair	0.081	12.398	fast
DC-brls	10	good	0.084	11.866	fast
DC-chl	5	fair	0.059	17.050	medium
DC-crl	3	poor	0.092	10.842	fast
DC-dhl	5	fair	0.044	22.906	medium
DC-drl	3	poor	0.110	9.076	fast
SN-ehl	4	good	0.331	3.018	very fast
SN-erl	4	fair	0.143	7.005	fast
SN-frl	4	poor	0.047	21.264	medium
SN-ghl	3	poor	0.025	40.091	slow
SN-grl	3	poor	0.052	19.087	medium
SN-hhl	5	fair	0.052	19.120	medium
SN-hrl	4	poor	0.100	10.049	fast

a model was assessed for each site as being either good, fair, or poor (see Table 2). This classification was made subjectively, based on the number of samples collected and the amount of fluctuation of DOC (rising and falling) during the recession period.

All sites responded differently in terms of how rapidly DOC was flushed from the soil, when this flush began, and how long it lasted. Slopes of the lines are indicative of how fast stored DOC was flushed from the upper soil reservoir, while the inverse of this slope refers to the time constant for each site (see Table 2). The time constants describe the amount of time (in days) it takes for the initial concentration of DOC stored in the upper soil reservoir to be decreased to about 32% of its initial value. Comparing time constants, the log-linear recession from each site (excluding anomalous site SN-ehl) was classified as being flushed at a fast, medium, or slow rate (see Table 2).

All lysimeters in the fast category were riparian lysimeters; conversely all sites in the slow category were hillslope lysimeters. This result indicates that the rate of flushing of DOC from upper subsurface soils is affected by topographic position. Lysimeters in the "fast" category were flushed, on average, in about 10 days. All of these sites are located near the streams in the riparian zone, suggesting that infiltrating meltwater passed through these soils at rates faster than soils at the other sites. All sites where the flush was classified as "slow" are hillslope lysimeters, with a mean response time of approximately 34 days. Such patterns could result from the fact that the transmissivity of the riparian soils is typically higher than the corresponding soils upslope, or may be due to differences in the rate of snowmelt.

Based on qualitative as well as quantitative observations, it appears that spatial and temporal patterns of snow accumulation and melt strongly affect the local timing of hydrological flushing. For example, site DC-arl was the first to be flushed, just as the discharge hydrograph began to rise. This site is located at the lowest elevation in the basin and receives lots of sunlight. At the other extreme, the snowpack lasted comparatively longer than usual at site B. Because this site is shaded from sunlight by the forest canopy, the initiation of snowmelt occurred later in the season and melt occurred more slowly.

Such observations account for the time constant associated with the recession of DOC in the stream channel being longer than the time constants describing the flush of DOC from the upper soil. Time constants describing the recession of DOC in the stream channels on the falling limb of the hydrograph were approximately 53 days for Deer Creek and 49 days for Snake River. During periods of snowmelt, significant streamflow is contributed from subsurface flow draining the upper soil reservoir. Because certain areas of the catchment initiate melt at different times and melt at varying rates, the chemical flushing of DOC source areas within the upper soil is staggered. This produces a protracted response of DOC concentrations in the stream.

In general, patterns observed in the upper 0.4 m soil were complex. The observations support the contention that spatial heterogeneities of the physical landscape are important determinants of DOC response. Because snow accumulation is not uniform and because snow melt over the catchment is asynchronous, patterns of DOC are strongly influenced by the spatial and temporal variation of precipitation, soil characteristics, and topography.

Contribution of DOC to streamflow from groundwater

The concentrations of DOC observed in the groundwater wells during baseflow (approximately 1.1 mg l^{-1}) were very similar to concentrations in Deer Creek, suggesting that groundwater is the source of in-stream DOC during conditions of low flow. It is thought that groundwater provides a steady source of DOC, albeit low in concentration, that accounts for DOC in the streams under periods of base flow. During snowmelt a rise in groundwater DOC on the order of 10 mg C l^{-1} was observed, correlated with increases in discharge. These results indicated that during periods of high flow, water from the upper soil is mixed with this shallow groundwater.

DOC concentrations in snow samples

Snowpack DOC samples were collected at sites A, B, C and E at a variety of depths on 14 January 1991. The samples ranged in concentration from 0.3 to 5.8 mg l^{-1}, with a mean of 1.3 mg l^{-1}. Snow samples collected from site B in both the riparian and hillslope locations at the bottom of the snowpack showed the highest concentrations in this range and were significantly higher in concentration than all other samples. Both of these samples were collected near the ground surface (12.7 cm from the soil), and both snow cores contained visible leaves and other particulate organic matter (POC). The high concentrations observed in these samples are considered to be artifacts of the soluble organic carbon leachate from this POC, resulting when the snow was melted, and is consistent with observations of McKnight *et al.* (1993). Excluding these two outliers, the average DOC concentration from all sites was 0.9 mg l^{-1}. On 21 May 1992, snow samples were obtained along Snake River at sites F and H, the only sites where snow remained. DOC ranged from 0.7 to 4.0 mg l^{-1}, with an average of 1.5 mg l^{-1}. Similar to earlier findings, a sample taken near the surface at site SN-hrl included visible quantities of POC, increasing the DOC concentration in the meltwater. Excluding this, the DOC average was 1.3 mg l^{-1}. In general, the average DOC concentration of the snowpack is low. Excluding all outliers described above, the overall average DOC concentration from all snow samples was 1.1 mg l^{-1}.

CONCLUSIONS

This research has shown that the major temporal variation of DOC in Deer Creek and in Snake River is determined by hydrological flushing of a variable source area of the catchment. Patterns of DOC in soil pore waters suggested that soils of the catchment are the primary source of DOC to streamflow. Field observations indicated that differences in the rate of flushing are likely influenced by variations in the transmissivity of soils, with riparian soils typically flushed at a faster rate and more frequently than hillslope soils. Variation in the amount of accumulated snow and asynchronous melting of the snowpack across the landscape caused the spring flush to be initiated at different times throughout the catchment, prolonging the response of DOC in the stream. These findings support the contention that spatial heterogeneities of the physical landscape are important determinants of DOC response. A valid quantitative theory for hydrochemical response of the system requires inclusion of the spatial and temporal variation of soil characteristics and patterns of snow accumulation and melt, in addition to topography.

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