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Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado

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Abstract. A quantitative understanding of the factors controlling the variation of dissolved organic carbon (DOC) in headwater streams is of scientific concern for at least two reasons. First, quantifying the overall carbon budgets of lotic systems is needed for a fundamental understanding of these systems. Second, DOC interacts strongly with other dissolved substances (heavy metals in particular) and plays an important role in the transport of contaminants.

In the Snake River near Montezuma, Colorado, measurements of DOC from 1980 to 1986 show rapid decreases in concentration from a peak very early in the snowmelt period. Peak DOC concentrations occur approximately one month prior to peak discharge in the stream. The decline in DOC with time is approximately exponential, suggesting that a simple flushing mechanism can explain the response. We examined hydrological mechanisms to explain the observed variability of DOC in the Snake River by simulating the hydrological response of the catchment using TOPMODEL and routing the predicted flows through a simple model that accounted for temporal changes in DOC. Conceptually the DOC model represents a terrestrial (soil) reservoir in which DOC builds up during low flow periods and is flushed out by infiltrating meltwaters. The model reproduces the main features of the observed variation in DOC in the Snake River and thus lays the foundation for quantitatively linking hydrological processes with carbon cycling through upland catchments. Model results imply that a significant fraction of the soils in the Snake River catchment contribute DOC to the stream during peak discharge. Our work represents one of the first attempts to quantitatively describe the hydrological controls on DOC dynamics in a headwater stream. These controls are studied through the model by imposing mass balance constraints on both the flux of water through the various DOC source areas and the amount of DOC that can accumulate in these areas.

Introduction

Allocthonous input of organic carbon is accepted to be an important process in headwater stream ecosystems (e.g. see Wallis 1979; Mulholland 1981). The importance of dissolved organic carbon (DOC) to this input also now is recognized (e.g. Schiff et al. 1990). Questions that remain open, however, are what source areas of a catchment are important in supplying DOC to a stream and what hydrological transport mechanisms are responsible for delivering DOC from the source areas to the streams.

In natural catchments, temporal and spatial variation in microclimatic variables and in vegetation and spatial variation in soils and bedrock will result in variability in both the DOC source areas and in the hydrological pathways. Nevertheless, for many small undisturbed catchments in the temperate zone it is useful to think in terms of a conceptual model in which the major source areas are: (1) the part of the regolith/bedrock that is below the perennial water table; (2) the riparian/hyporheic zone; and (3) the upland soils, which are usually unsaturated but which conduct subsurface flow during rainstorm and/or snowmelt periods. Hydrological pathways are associated with each of these zones. The questions posed above then can be phrased in terms of which combinations of source areas/flow paths are responsible for delivering DOC to the stream under different hydrological regimes.

At one extreme, DOC produced in the upland areas of the catchment and modified by soil processes might not directly affect stream concentrations because transport pathways are through soils that strongly sorb DOC (Wallis 1979). Alternatively, one might conceptualize that the 'variable source area' mechanism of streamflow generation in catchments plays a leading role in determining temporal variation of DOC in headwater streams. In this scenario, high levels of DOC in soil waters would be flushed out into the stream as the local water table rose during storm and snowmelt events. In addition, during wet periods DOC might be transported along preferred flow paths (e.g. macropores) from upland hillslope soils to the stream (Fiebig et al. 1990).

In catchments in the Rocky Mountains in which the hydrological year is dominated by the Spring snowmelt event, the relation between DOC and discharge is not a simple correlation; rather, the peak DOC concentrations occur well before peak discharge with continuously (and rapidly) declining concentrations as snowmelt proceeds (Denning et al. 1991). Such behavior qualitatively can be attributed to flushing of a soil DOC pool by infiltrating meltwater (Lewis & Grant 1979; Baron et al. 1991), although spatial variability in soils coupled with asynchronous melting of snow within a catchment due to differences in elevation and aspect across the terrain may contribute to the earliness of the flush (Denning et al. 1991). Others have suggested that a flushing mechanism may explain some of the observed variation in DOC concentrations in catchments outside the Rocky Mountains as well (e.g. Foster & Grieve 1982).

We present data for the Snake River near Montezuma, Colorado that shows the distinctive 'flushing' response of DOC during the hydrologically dominant snowmelt event. The data show an exponential decline in the concentration of DOC in the stream across the snowmelt hydrograph, suggesting that the conceptual model of meltwaters flushing a terrestrial store of DOC is a reasonable explanation of the data. We applied relatively simple hydrological and chemical mixing models to describe the transport of DOC to the Snake River.

Because of limits on the available data, we recognized at the outset that we would not be able to definitively answer the question 'what are the hydrological mechanisms that contribute to DOC variation in the Snake River?' Rather, we sought to examine whether the flushing hypothesis (Lewis & Grant 1979; Denning et al. 1991) was *quantitatively consistent* with results from a mathematical model of catchment hydrology. Our model results led us to speculate that flushing from a terrestrial (soil) sources is the most important mechanism affecting DOC concentrations in the Snake River. The levels of soil DOC and the spatial extent of areas contributing DOC to the stream calculated by the model are consistent with observations made elsewhere and with generally accepted views of catchment hydrology. These calculated entities offer a basis for further testing the hypothesis by measuring temporal changes in soil DOC levels and in contributing areas.

Site description

The site of the study is the Snake River above its confluence with Deer Creek (Fig. 1). The catchment, near Montezuma, Colorado, is mountainous ranging in elevation from about 3350 m to 4120 m. The Continental Divide bounds the catchment on the south and east. Approximately half of the catchment is above the tree line.

The catchment is underlain mainly by the Precambrian rocks of the Idaho Springs Formation and, in lesser amounts, by the Swandyke hornblende gneiss and the Silver Plume Granite (Lovering 1935). Alluvial deposits fill the valley bottoms and a bog iron ore deposit occupies a part of the upper valley (Lovering 1935).

The Snake River originates in a glacial cirque. In the uppermost reaches sedges and grasses are abundant and extend halfway up the steep slopes. The valley floor is flat and wide, some 250 to 500 m across in the upper two-thirds of the catchment above our sampling point. In the upper third of the catchment, the riparian zone is marshy and vegetated with sedges and willows. In the central third of the stream, willows predominate in the riparian zone, pine forest covers the upper slopes, and sedges are abundant between the riparian zone and the forest. In the lower third of the stream the pine forest extends to the stream banks and the stream gradient is steeper than in the upper reaches. There are two large beaver ponds located at the transition from willows to pines in the riparian zone.

Methods

Data. Data on chemical composition of streamwater were collected over the period 1980 to 1986 (McKnight & Bencala 1990); similar data were collected during 1991. Samples were taken on the Snake river immediately above the

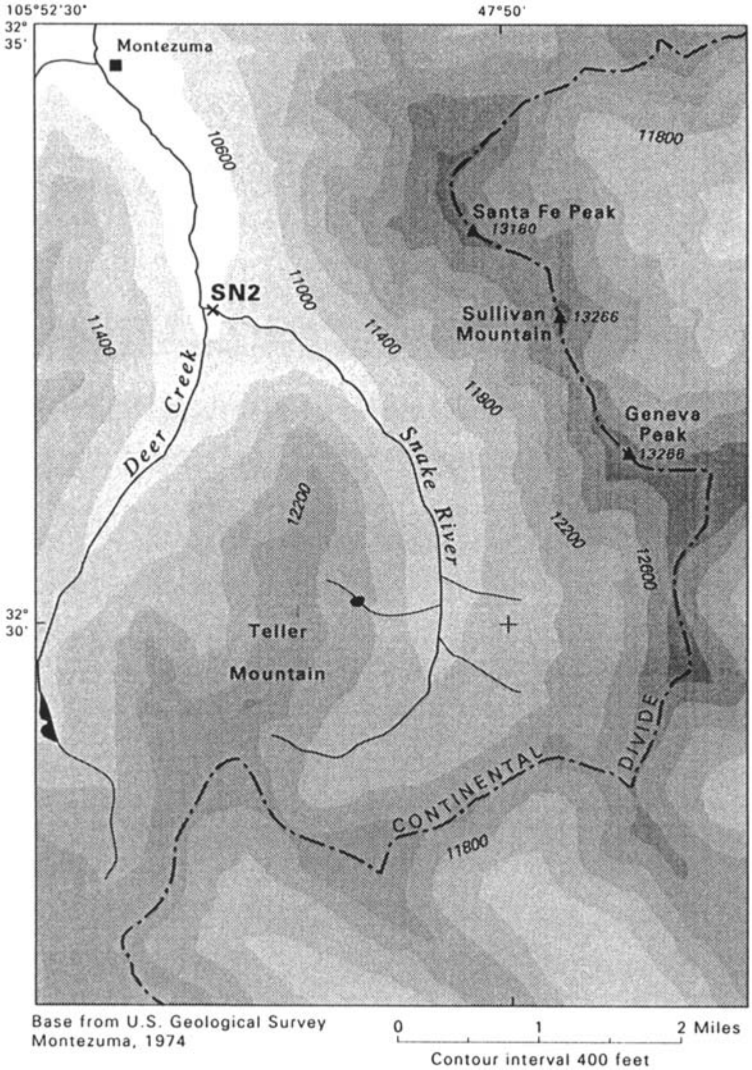

Fig. 1. Location map for the site on the Snake River.

confluence with Deer Creek (Fig. 1) at site SN2. DOC samples were filtered through 0.45 µm Selas silver membranes with a stainless steel Gelman filtration unit and stored at 4 °C in glass until analysis. DOC concentrations were measure on a Technicon* carbon analyzer or on a Dohrman carbon analyzer.

* Use of brand names in this article is for identification purposes only and does not constitute endorsement by the US Geological Survey.

Discharge of the Snake River at the site SN2 (Fig. 1) was measured periodically using the velocity-area method. A pygmy current meter was used to measure velocities.

Daily discharge values for the Snake River near Montezuma, Colorado (about 10 km downstream of the SN2) were retrieved from US Geological Survey records. Daily precipitation and minimum/maximum temperatures for a meterological station at Dillon were retrieved from the NOAA Climatological Data Summary. Elevation data (digital elevation model data) for the Montezuma quadrangle were obtained from the National Mapping Division of the US Geological Survey.

Hydrological modeling. We applied the hydrological model TOPMODEL (Beven & Kirkby 1979) to the Snake River catchment. TOPMODEL is, in a sense, not a single model, but a conceptual framework; the main ideas behind TOPMODEL can be incorporated into many conceptualizations of the catchment hydrological cycle. In fact, this has been done in that there are many versions of TOPMODEL in use with rather different treatments of details of the computations. They all have the treatment of topography introduced by Beven & Kirkby (1979), however. Most important, all use a topographic index, derivable from topographic data, that encapsulates the important hydrological driving mechanisms for flow. The index uses a ratio of the area above any point on the catchment that drains to the point (a measure of how much water is funneled toward a point) to the local slope at that point (a measure related to the rate at which water can be transported downslope from the point). See Beven & Wood (1983) for a complete description of the model.

Added to the formulations of the topography are the other standard components of the water budget – e.g. evapotranspiration, snowmelt, channel routing. We use the evapotranspiration formula of Hamon (1961) and a snowmelt model that takes melt to be proportional to temperature, with the melt coefficient varying seasonally (see Bras 1990). We treat the catchment as a whole and ignore channel routing in the present application.

TOPMODEL calculates not only the stream hydrograph but information that is useful for linking hydrological calculations to hydrochemical models (Cosby et al. 1987). For our purposes (see below), it is important that TOPMODEL calculates subsurface flow, overland flow, and saturation deficit (depth to water table).

The topographic index was calculated from digital elevation model data using the programs of Jenson & Domingue (1988) and of D. M. Wolock (unpublished). Average soil depth was assumed to be 1 m; an 'upper horizon', the presumed reservoir for high DOC levels, was taken to be 0.6 m thick (see discussion of the DOC model below).

A continuous record of daily discharge at the sampling site SN2 was extrapolated from the infrequent pygmy meter measurements through a regression of these measurements on the measure flow at Dillon on the same days.

This extrapolated record was used as the measured discharge from the catchment in calibrating TOPMODEL to the Snake River at SN2.

Precipitation for the site at Dillon (elevation 2767 m) was adjusted by assuming an increase in precipitated snow with elevation of five inches per thousand feet (Leavestly, pers. comm.). This assumption is apparently a reasonable 'rule of thumb' for the area as judged by snow course data obtained in the Spring of 1991 on St. Kevin Gulch near Leadville, Colorado (J. W. Harvey & N. S. Spahr, pers. comm.). In warmer months, rainfall was adjusted by applying an increase of four inches per thousand feet. This results in an overall annual catchment yield of about 70% for 1984, a proportion that is reasonable for the Colorado Rocky Mountains (G. W. Leavesley, pers. comm.).

Temperature records are used in our version of TOPMODEL to compute potential evapotranspiration (Hamon 1961) and to calculate snowmelt by a temperature index method (Devar 1970; E. A. Anderson, as cited in Bras 1990). Temperatures were adjusted for elevation using the moist adiabatic lapse rate for the correction (e.g. see Morris 1985), i.e. by subtracting 5 °C from the measured temperatures at Dillon. The median elevation of the catchment is approximately 11700 feet whereas the elevation of the meterological station is 9070 feet.

TOPMODEL was calibrated for the Snake River using the Rosenbrock optimization algorithm. (See Hornberger et al. 1985 for a description of the use of the Rosenbrock method in conjunction with TOPMODEL.) The parameters optimized were two soil parameters, one intended to represent the rate of decrease of hydraulic conductivity with depth divided by porosity and the other the hydraulic conductivity of the surface soil (see Beven & Wood 1983), and one snowmelt parameter, the threshold temperature for melting.

Chemical modeling. The conceptual model is that DOC in riparian and hillslope soils is 'flushed out' by the formation of a ground-water ridge during periods of snowmelt (Figs. 2a, 2b). This dissolved organic material (DOM) in the upper soil horizons is probably chemically different in several ways from that in the deeper ground water.

DOC is treated in our model as a single entity; however, it is important to recognize its inherent chemical diversity. The myriad organic compounds which comprise DOM can be classified based upon their hydrophobic or hydrophilic properties and as organic acids, organic neutrals, and organic bases (Leenheer & Huffman 1979). Fulvic acid, which in the fractionation procedure of Leenheer and Huffman are hydrophobic acids, are typically a major class (20–80% of the DOC). The relative distribution of DOM between the classes can vary with depth in the soil (Cronan & Aiken 1985; Cronan 1990) and within each class there may be significant chemical differences. For example, fulvic acid that is in deeper ground water may represent the fraction of the source fulvic acid that is not readily sorbed by aquifer material, and may have a lower aromaticity and a lower carboxylic acid content than the

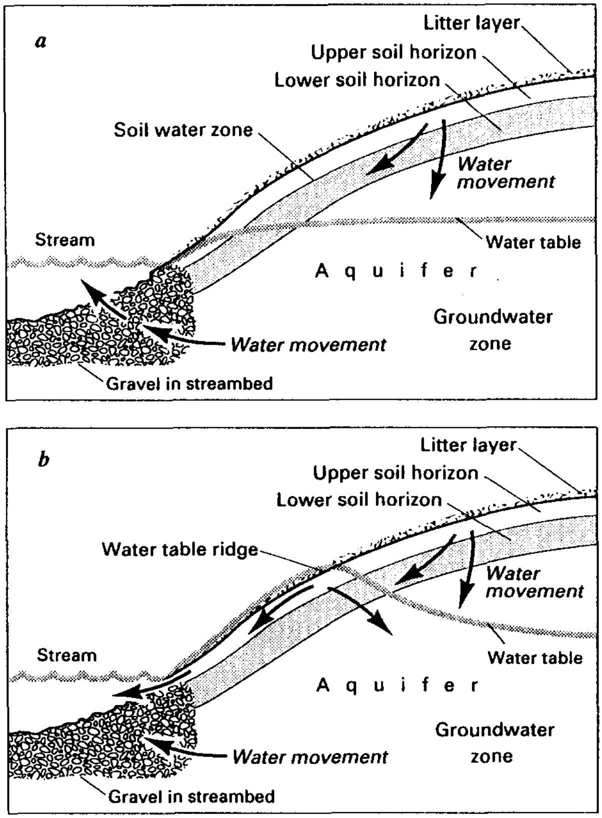

Fig. 2. Schematic diagram of the mechanism of soil-water flushing: (a) under low baseflow conditions, subsurface flows are through lower soil horizons; (b) under high flow conditions, the water table is elevated and water flows toward the stream through upper as well as lower horizons.

source material. The part of the DOM that is biologically labile (readily used as a substrate by microorganisms) probably varies significantly between subsurface zones as well. DOM coming from the upper soil zone may include fresh leachates from the litter layer that are better microbial substrates than found in deeper ground water.

Our chemical model is based on a simple constraining equation implied by conservation of mass. That is, the hydrological model constrains mass balance by requiring that the total stream discharge be a sum of the contributions to the stream: overland flow and subsurface flow.

$$\mathrm{Flow}_{\mathrm{stream}} = \mathrm{Flow}_{\mathrm{overland}} + \mathrm{Flow}_{\mathrm{subsurface}},$$

or, because we distinguish between flow through upper and lower soil layers,

$$\text{Flow}_{\text{stream}} = \text{Flow}_{\text{overland}} + \text{Flow}_{\text{upper soil}} + \text{Flow}_{\text{lower soil}}.$$

The chemical mass balance is then

$$c_{\text{stream}}\text{Flow}_{\text{stream}} = c_{\text{overland}}\text{Flow}_{\text{overland}} + c_{\text{upper soil}}\text{Flow}_{\text{upper soil}} + \\ + c_{\text{lower soil}}\text{Flow}_{\text{lower soil}}.$$

By using the hydrological model to determine the flow components ($\text{Flow}_{\text{overland}}$, $\text{Flow}_{\text{upper soil}}$, and $\text{Flow}_{\text{lower soil}}$), and assuming that c_{overland} and $c_{\text{lower soil}}$ are constant through time and known (measured) quantities, we can calculate the stream concentration if we can model the concentration in the upper soil. This process is described more fully below.

Despite the potential overall complexity of the entire process, a simple interpretation of the conceptual model is that DOC in the vadoze zone builds up during periods of low flow due to microbial activity in the absence of flushing and that this DOC is pushed out into the stream during periods of high flow. Such a conceptual model indicates that concentrations of DOC in water flowing from the soil to the stream should be high in the initial part of a rainstorm or snowmelt period and then decrease as meltwaters continue to flush the zone formerly above the water table but now exposed to significant streamward flow of water.

An embodiment of the simplest mathematical representation of flushing such as envisioned in the conceptual model is a continuously stirred tank reactor (CSTR). We constructed a simple mixing model, based on a CSTR, to explain temporal variation of DOC concentrations in the Snake River. We envision two reservoirs – one representing the 'upper soil' and one representing the 'lower soil' (Fig. 3). Flows through the two reservoirs are apportioned on the basis of results from TOPMODEL. TOPMODEL calculates total subsurface flow, $\text{Flow}_{\text{subsurface}}$. TOPMODEL also calculates the saturation deficit (the amount of water necessary to cause the water table to rise to the ground surface). The saturation deficit can be used to apportion the total subsurface flow ($\text{Flow}_{\text{subsurface}}$) into components: flow through the lower soil compartment ($\text{Flow}_{\text{lower}}$) and flow through the upper soil compartment ($\text{Flow}_{\text{upper}}$). If the calculated saturation deficit (S) for the catchment is greater than $n*z_{\text{upper}}$ (where 'n' is the soil porosity and z_{upper} is the depth of the upper soil), then the water table is below the upper soil layer and all of the flow is through the lower layer. If, on the other hand, the calculated value of S is less than $n*z_{\text{upper}}$, the water table is within the upper reservoir. In that case we use a simple proration to apportion flow to the upper reservoir.

$$\text{Flow}_{\text{upper}} = \text{Flow}_{\text{subsurface}} *(n*z_{\text{upper}} - S)/(n*z_{\text{total}} - S). \tag{1}$$

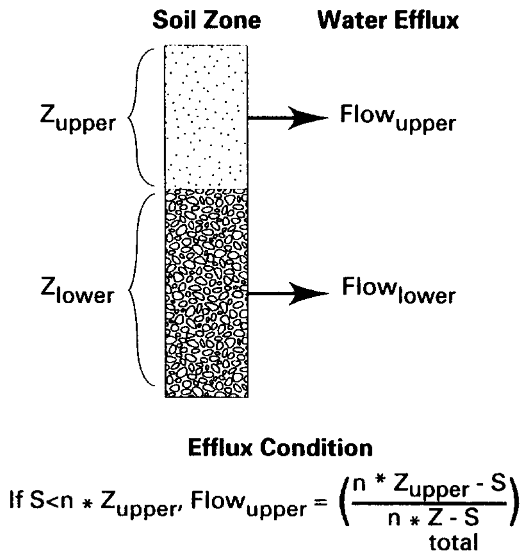

Fig. 3. The conceptual model for describing DOC dynamics uses two soil stores, a 'lower' and an 'upper' compartment. DOC is stored in the upper compartment during low-flow conditions and released from this compartment during high-flow conditions.

F_{lower} is then just the difference between the total subsurface flow and the flow through the upper compartment. Note that the important concept is assigning a fraction of the flow to the upper compartment. The total depth for flow, which we have taken to be 1 m, is in reality much greater when consideration is given to flow through the fractured bedrock. The critical aspect of our simulations, however, is not the exact depth of the lower compartment which is assigned a constant DOC concentration, but the percentage of flow routed through the dynamic upper compartment. Our algorithm is a convenient way to apportion the flow.

We assume that DOC in the lower reservoir is constant at 1.2 mg/L to approximate the low-flow values observed in the stream. To account for build-up of DOC in the soil, we use the model of Grieve (1991). DOC in the upper reservoir varies according to

$$\begin{aligned} DOC_{upper}(t + 1) &= DOC_{upper}(t) + a*10^{0.04T} \\ &- (1 - e^{-kT})*DOC_{upper}(t) \\ &- (1 - Flow_{upper}(t)/V_{upper}(t))*DOC_{upper}(t) \end{aligned} \quad (2)$$

where t indicates time, T is temperature, a and k are rate constants for evolution and decay of DOC and 0.04 is a fixed constant (see Grieve 1991), $Flow_{upper}$ and V_{upper} are, respectively, the flow through and wetted volume of the upper soil reservoir, and the time step is one day. (The wetted volume is the volume below the water table; it is calculated as the difference between the total pore volume of the upper compartment minus the saturation deficit.) Although the appropriate temperature is a soil temperature, we used air temperature as a surrogate. Grieve used a value of k that would give a decay half time of about 1 month at 10 °C. We followed this assumption and used k = 0.002. We then chose a value of a (= 0.10) and a value for z_{upper}(0.6 m) to give a reasonable representation of the peak of the DOC value observed in the Snake River during early snowmelt.

The DOC in the stream is calculated as a simple mixture of waters from direct snowmelt and from the upper and lower soil reservoirs:

$$DOC_{stream} = (Flow_{overland} * DOC_{snow} + Flow_{upper} * DOC_{upper} + Flow_{lower} * DOC_{lower}) / Flow_{total}. \quad (3)$$

We took DOC_{snow} to be constant at 1 mg/L based on a measurement of pristine snow in the area (McKnight et al. 1993).

Results

Temporal variation of DOC. Peak DOC concentrations in the Snake River occurred well before peak discharges (Fig. 4). The relationship between DOC and discharge is not simple, as a scatter diagram shows (Fig. 5). Thus, the simple mixing approach to describing the temporal variation of DOC in the stream (Johnson et al. 1969) is not valid, although there is a tendancy for higher values of DOC to be associated with higher discharges.

A clue to a conceptual model for the DOC response observed in the Snake River can be gleaned from the form of the temporal decline in DOC: an exponential decline suggests that a CSTR (see above) from which DOC is flushed into the stream is a reasonable postulate. Such an exponential decline is reflected in straight line segments on a semilogarithmic plot of DOC versus time (Fig. 6). This observation is the basis for our mathematical model for DOC response.

Hydrological model. We focus our attention on modelling on the snowmelt period for 1984. We decided against 1980 and 1981 because the concentration data were relatively sparse, with samples taken at approximately two-week intervals. The years 1982, 1985, and 1991 proved to be unworkable for modelling because our crude approximations for extrapolating measured precipitation at Dillon across the entire high-elevation catchment failed for these years. That is, the runoff indicated that approximately twice as much snow must have fallen in the catchment than we estimated by extrapolation from measurement at Dillon. This clearly indicates the need for improved estimates of snow water content and coverage for modelling precipitation-runoff rela-

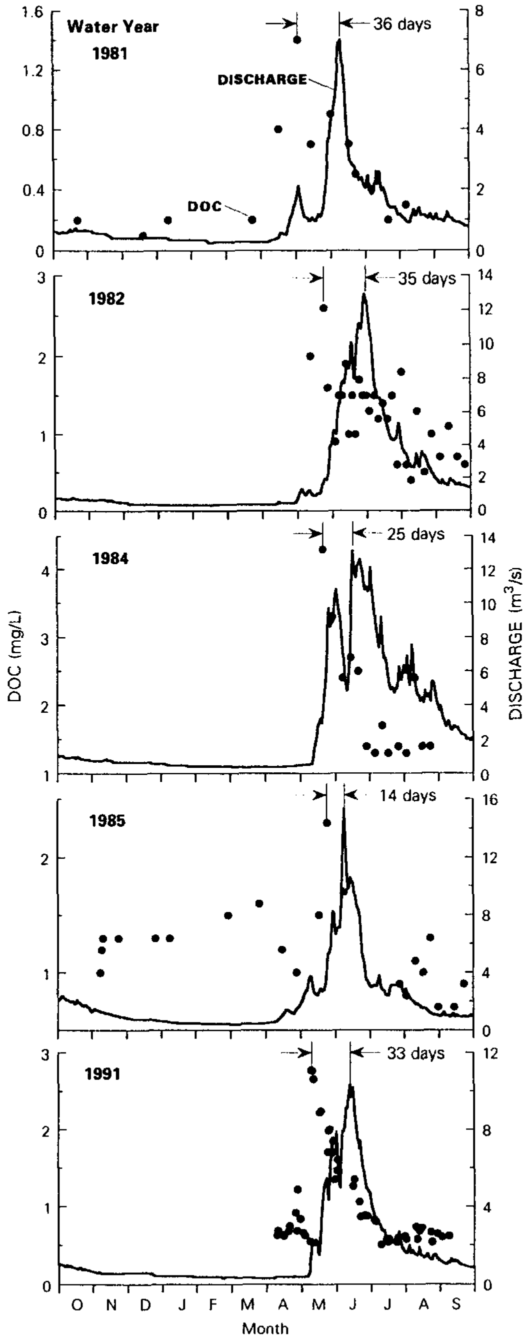

Fig. 4. Peak concentrations of DOC in the Snake River occur on the ascending limb of the snowmelt hydrograph, well before peak discharge.

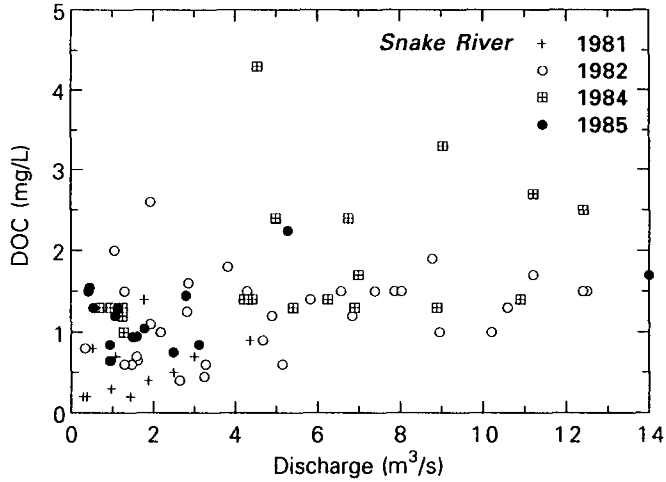

Fig. 5. Concentrations of DOC in the Snake River do not show any smooth, consistent relationship to discharge.

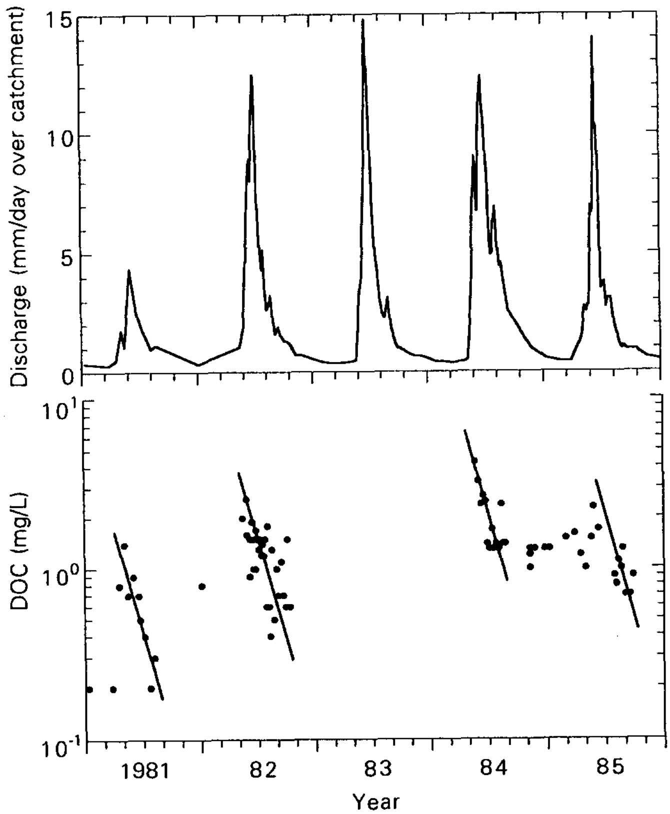

Fig. 6. The concentrations of DOC in the Snake River tend to decrease exponentially with time over the course of the snowmelt event.

tionships for mountainous catchments. While we could develop good simulations of stream discharge by an *ad hoc* adjustment of precipitation, we decided against this approach. Thus we concentrated our efforts on 1984. Because we intend to demonstrate the concept rather than provide a definitive model, this focus is not a serious deficiency.

The general shape of the snowmelt hydrograph for 1984 simulated using TOPMODEL is in accord with the measured hydrograph (Fig. 7). The initial timing of the hydrograph rise is late in the simulated hydrograph; presumably, the temperature index model calculates the initiation of significant snowmelt to be later than when the melt is actually initiated. This may be due to errors introduced in our temperature extrapolation procedure, or, more likely, may be due to the exclusion of asynchronous and spatially heterogeneous melting in the simple model that we use. The remainder of the simulation follows the observed hydrograph quite well although the late part of the recession of overpredicted. Overall we consider this simulation to be quite reasonable given the limitations in the data (e.g. the need to extrapolate the discharge, precipitation, and temperature data from downstream stations).

Most of the simulated flow is routed through the deep subsurface, but significant flow during snowmelt periods does occur through the upper soil reservoir (Fig. 8). Pulses of overland flow are also simulated.

Chemical model. The simulated hydrological response for 1984 was used as input to our simple DOC model. The simulated DOC response provides a reasonable reproduction of the observed dynamics (Fig. 9) although there is an apparent 'delay' in the DOC response. That is, the early value of high DOC is underestimated by the model because the initial hydrograph rise is late in the simulated flow (see above). The model does mimic the sharp decline in DOC concentrations in the stream after an initial peak early in the melt hydrograph.

The model also calculates values for variables that are related to the catchment itself rather than the stream. The simulated concentrations of DOC in the upper soil reservoir range from about 9 mg/L to 29 mg/L (Fig. 10) over the course of the year. The soil reservoir directly reflects the build-up of DOC during low-flow months and the flushing during the snowmelt. The information from TOPMODEL on the spatial distribution of water-table height furnishes a picture of the spatial extent of the DOC source areas. Whenever the water table is in the upper soil horizon, our model calculates DOC transport to the stream. The percentage of the catchment contributing DOC varies from 10% to 100% on an average weekly basis over the year (Fig. 11). During the peak of the snowmelt, the entire catchment contributes to the streamward transport of DOC. These figures for the contributing areas are maximal in that we count an area as contributing if the water table is just barely in the upper zone (i.e. if the local saturation deficit, S_i, is less than $n*z_{upper}$). Thus, even during low flow conditions, we simulate a portion of the near stream catchment as contributing DOC from the upper reservoir.

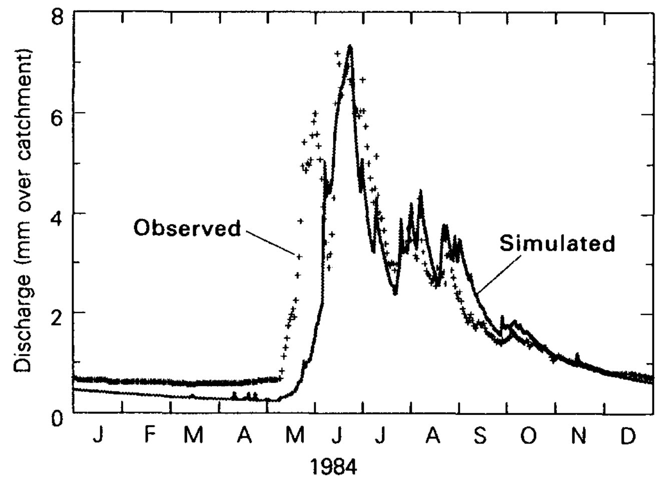

Fig. 7. The hydrograph for the Snake River at SN2 as extrapolated from measurements from a stream gage near Montezuma, CO and the simulated hydrograph from TOPMODEL.

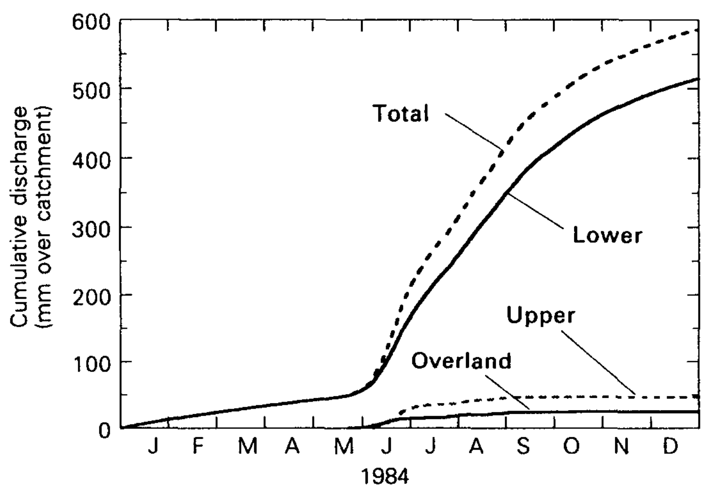

Fig. 8. Components of the simulated hydrograph: overland flow, flow through the upper compartment, flow through the lower compartment, and total flow.

Discussion

A quantitative understanding of the factors controlling the variation of DOC in headwater streams is of scientific concern for at least two reasons. First, quantifying the overall carbon budget of lotic systems is needed for a fundamental scientific understanding of these systems. Second, DOC interacts

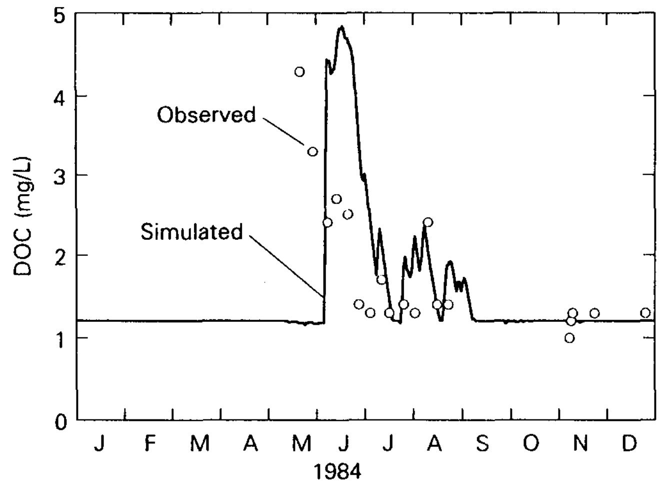

Fig. 9. Simulated DOC concentrations for the Snake River. Note that the lateness of the simulated peak is due to the lateness of the snowmelt as calculated by TOPMODEL.

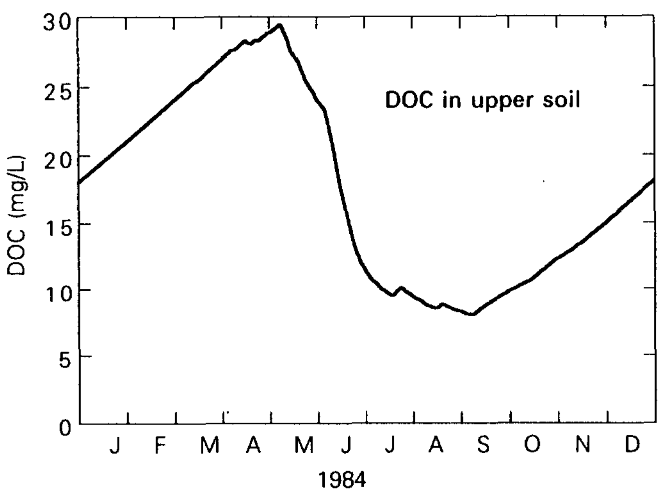

Fig. 10. Simulated DOC concentrations in the upper soil compartment.

strongly with other dissolved substances (heavy metals in particular) and therefore plays an important role in the transport of contaminants in streams.

In the Snake River and in Deer Creek near Montezuma, Colorado, measurements of DOC over the snowmelt period show rapid decreases in concentration from a peak very early in the melt event (on the ascending limb of the hydrograph). This type of behavior is not typical for mixing of waters from a relatively constant-concentration (ground-water) reservoir with waters from rain or snowmelt. For example, sulfate concentrations in the Snake River show the more typical dilution response, with the lowest concentrations at high flows and vice-versa. The dilution response is confirmed by the hyperbolic relationship between concentration and discharge (Fig. 12) which results in the linear relationship of Johnson et al. (1969). The contrast between the

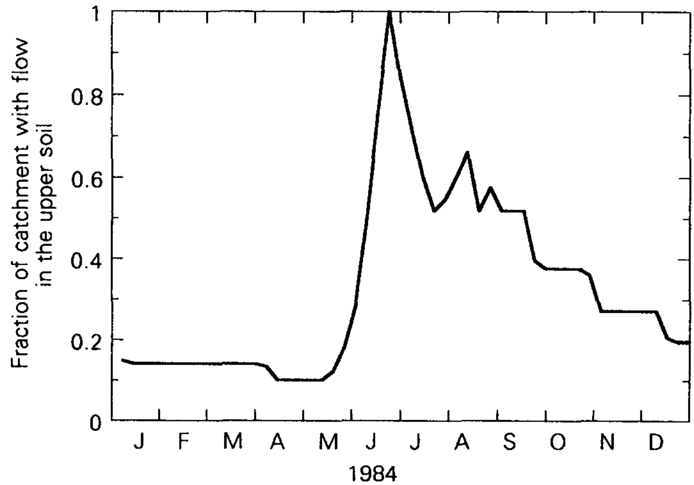

Fig. 11. Weekly average of the percent of area of the catchment contributing DOC from the upper soil compartment to the stream as calculated by TOPMODEL.

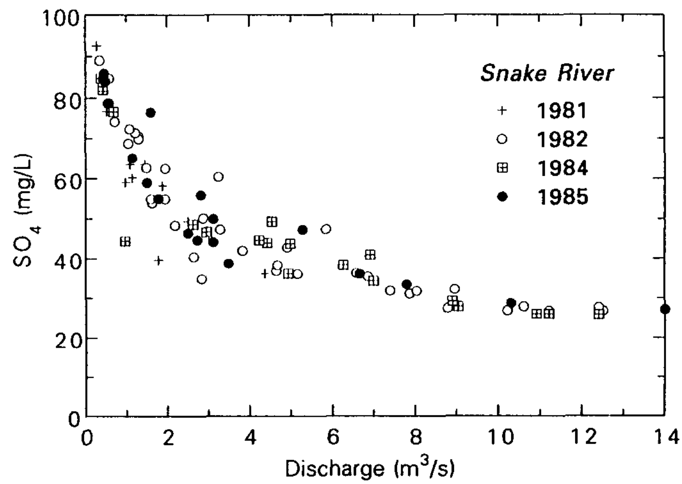

Fig. 12. The concentrations of sulfate in the Snake River are rather closely related to discharge (a hyperbolic relationship) suggesting a simple dilution of a subsurface store with snowmelt waters.

behavior of sulfate (Fig. 12) and that of DOC (Fig. 5) reflects the dramatic effect of a variable-concentration soil reservoir on the behavior of DOC.

We have postulated a vary simple model to describe the major features of the temporal variation in DOC concentrations over the snowmelt period in the Snake River, a model of a continuously stirred tank reactor, to describe the observed dynamics. Conceptually the model can be taken to represent a terrestrial (soil) reservoir in which DOC builds up during low flow periods and is flushed out when infiltrating meltwaters cause the water table to rise into this 'reservoir'. The model is similar in emphasis to that of Greive (1991) but uses a topographically controlled hydrological model to drive the flushing of the soil store. Robson & Neal (1991) successfully used TOPMODEL with a simple mixing model to compute temporal changes in acid neutralizing capacity (ANC) in the Hafren, a stream in Wales. ANC can be taken to be a conservative tracer in the Hafren. Our work indicates that the approach can also be used effectively to model the behavior of a non-conservative substance such as DOC, with the source and sink terms represented by the simple model of Grieve (1991).

Neither the simulated discharges from TOPMODEL nor the simulated DOC values from the CSTR model can be considered to be even nearly perfect representations of the data. Nevertheless, we conclude that the model results are broadly consistent with the available data. That is, despite the simplicity of the model, it captures the essence of the observed variability. Given the available data, we cannot reject the model as a valid description of processes occurring in the Snake River/Deer Creek system.

Does a terrestrial source of DOC exist within the Snake River/Deer Creek system and, if so, where is it? Our analysis for the Snake River postulates a terrestrial source for DOC with concentrations in the 9–29 mg/L range. While we have no measurements of DOC in soil water from the Snake River to confirm this calculation, we note that the average concentrations of DOC from soil lysimeters in the Loch Vale, Colorado catchment are reported to be 19 mg/L by Denning et al. (1991). We plan to test this aspect of the model calculations in the future by making direct measurements of soil DOC in the Snake River catchment, but the results reported by Denning et al. (1991) suggest that the model calculations are within the expected range. Our simulations also suggest a fairly well distributed source for DOC to the stream – soils over a significant portion of the catchment where the saturation deficit declines to the point that indicates that the water table has risen sufficiently to flush the zone where DOC levels are high in the Spring (Fig 11). We have no quantitative assessment of the agreement of actual contributing areas with those simulated by TOPMODEL, but anecdotal information again suggests that the simulation results are reasonable. We have observed (June 1991) saturated (or near saturated) conditions in the Snake River catchment well upslope from the stream. Leavesley (pers. comm.) has observed such conditions on hillslopes nearly up to the divides in several Rocky Mountain catchments.

The CSTR model for flushing implicitly incorporates the notion that DOC should decline exponentially during periods of high flow. (This is the nature of a one-compartment linear model when the dominant process is flushing.) The data for the Snake River over the major snowmelt period suggest that such an exponential decline is in fact reasonable (Fig. 6).

We conclude that the linked hydrological and chemical models presented in this paper are quantitatively consistent with the conceptual flushing model. This successful simulation in the variation in stream DOC in the Snake River lays the foundation for incorporating hydrological information into studies of carbon cycling through upland catchments. Future work should be aimed at testing the assumptions implicit in this model, at refining the description of processes that the model seeks to describe, and at improving the model as better data become available.

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