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## Solute transport along stream and river networks

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### Introduction

Since the 1950s, the science of solute transport in streams has burgeoned. Significant advances have been made in our understanding of the controls on solute transport at the reach scale (hundreds of metres), but few studies have scaled beyond continuous reaches of a few kilometres. Notable exceptions include theoretical studies of solute transport throughout river networks (e.g. Zhan, 2003; Zhang and Aral, 2004; Lindgren *et al.*, 2004; Gupta and Cvetkovic, 2002). Laenen and Bencala (2001) summarize a number of reach-scale stream-tracer experiments throughout the Willamette River basin in Oregon, and there have been recent efforts to examine the factors controlling the transport of nitrogen through the entire Mississippi River basin (Alexander *et al.*, 2000) and of large, Arctic river networks (Holmes *et al.*, 2000). These latter studies generally rely upon discharge-monitoring data, potentially lumped both in space and time (i.e. a single value to represent a basin and a single annual-discharge estimate) and water-quality

data throughout respective basins. Thus, our current understanding of solute transport at the river network scale is limited.

In this chapter, we focus on the processes that control solute transport in rivers and explore how those controls change from headwaters to higher-order streams. Fluvial geomorphologists have long studied how channel geometry and resulting hydraulics change predictably along the network continuum (Leopold and Maddock, 1953). We propose that the predictable changes in morphology and hydraulics have predictable impacts on the physical processes of stream-solute transport. This issue is critical to understanding stream ecology and contaminant transport at the network scale. For example, network-scale solute transport is important to conceptual ecological models, such as the River Continuum Concept, that propose ecosystem processes and forcing factors along streams vary systematically with location along the river due to changes in river size and connectivity to the adjacent landscape (Vannote *et al.*, 1980; Fisher *et al.*, 1998). Thus, we have structured this chapter to open with an introduction of solute-transport processes in streams (see Fischer *et al.* (1979) and Rutherford (1994) for additional details). We then link these processes to morphologic and hydraulic domains within the stream network. Finally, we offer a perspective on future research foci that will improve our understanding of solute transport from headwater streams to large rivers.

## Review of current knowledge

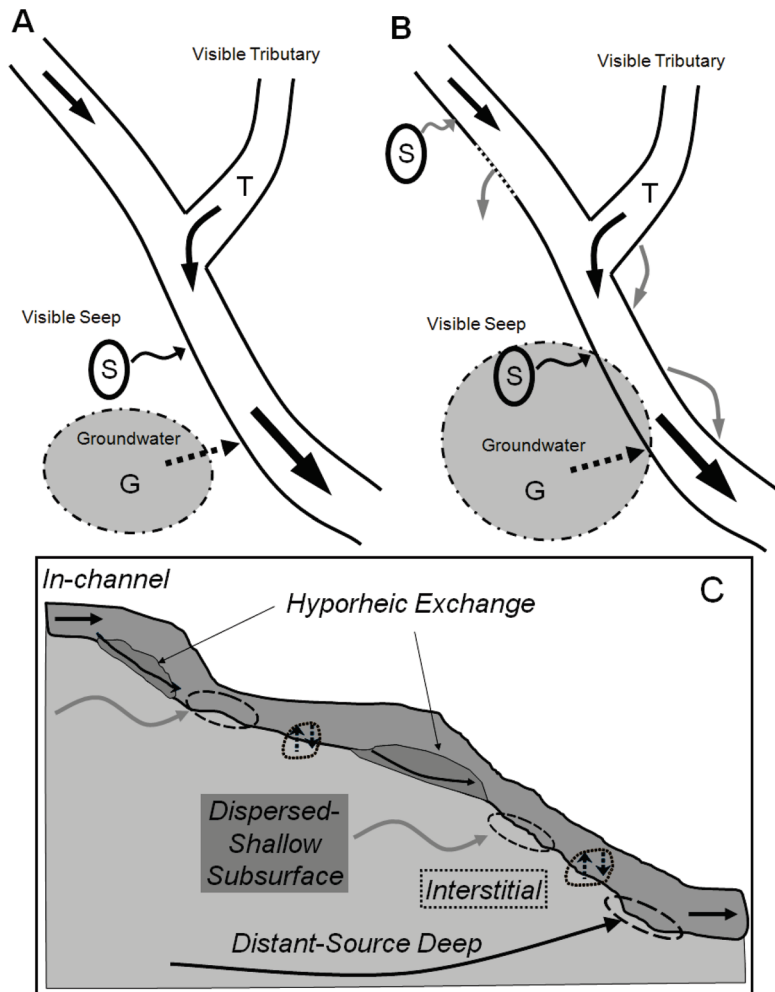
Material transport in streams is influenced by two major categories of processes: physical and chemical, where the latter may include geochemical and biochemical reactions. Here, we mostly focus on the physical hydrological controls on the fate and transport of dissolved materials (solutes). We do not address the larger field of biogeochemistry directly but rather show how hydrological processes influence the potential occurrence of a variety of biogeochemical transformations. Much of the basic knowledge about solute transport is derived from experiments in which tracer solutes are released into streams and their movement monitored at one or more sampling points downstream. Consequently, transport processes of solutes, especially conservative or non-reactive solutes, through short sections of stream networks are relatively well understood. In contrast, the movement of particulate (e.g. viruses or bacteria), sediment-sorbed (phosphorus), colloidal (trace metals) or immiscible (oil) contaminants is poorly known. Sources of most solutes in streams are found across landscapes, proximal and distal from the stream network. The hydrologic connections between landscapes and stream networks control the source amounts and fluxes of solutes to streams. Further, the transport of some contaminants occurs in several phases simultaneously. For example, Montana's Clark Fork was initially contaminated by erosion and the redistribution of mine tailings throughout large portions of the stream network. Today, trace-metal transport

occurs both in dissolved and colloidal forms (Nimick *et al.*, 2003). Additionally, during high flows, erosion continues to transport and redistribute sediment within the stream network. A thorough review of these complexities, for a multitude of contaminants, is beyond the scope of this chapter.

There are four physical hydrologic processes that strongly affect the transport of solutes in stream networks: advection, dispersion, transient storage and the mixing of stream water with inflows (Ramaswami *et al.*, 2005). The processes of longitudinal advection and dispersion are well known and commonly described by one-dimensional transport models. In these models, 'transient storage' refers to the movement of channel water and associated solutes into either in-channel dead zones or subsurface flowpaths of the hyporheic zone (Harvey and Wagner, 2000). The process of mixing with inflows refers to (1) groundwater–surface-water exchange with local or regional aquifers (gaining or losing reaches), at a spatial and temporal scale beyond hyporheic exchange, and (2) tributary junctions throughout the stream network, where waters from different parts of the network are combined. In the context of stream-solute transport, research has focused on shorter reaches (100–1000 m in length) because they (1) are of appropriate size to contain channel heterogeneity, (2) represent particular morphologies or stream types, (3) are easily comparable to similar channel lengths of different stream types and (4) represent a scale that is tractable for current methods and reasonable field-research logistics.

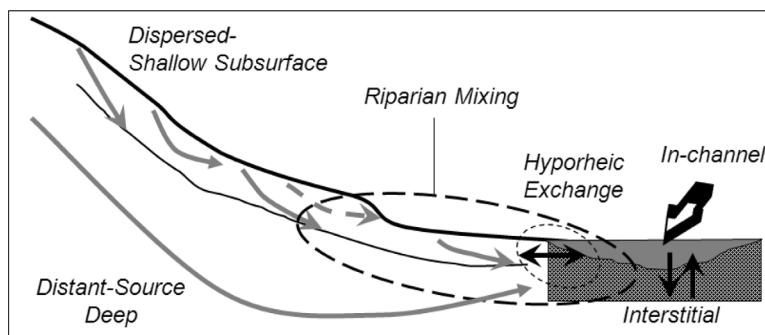
The movement of water through landscapes and down stream networks links a variety of potential sources and sinks of solutes throughout watersheds. The spatial distribution of landscape elements within watersheds (including land use types) and their connection to the hydrologic network will largely control the movement of water and solutes between stream networks and the catchment. For example, runoff from urban lands is likely to be flashy – reflecting rapid response to hydrologic inputs – and likely to provide a mix of solutes foreign to streams in less human-affected settings. Alternatively, irrigation demand removes both water and associated solutes from streams and applies those waters and solutes across portions of the watershed. Thus, distributed sources and sinks of contaminants or other solutes to streams exist throughout watersheds (Todd *et al.*, 2003).

The delivery of solutes to streams occurs via a complex mixture of point-source inflows (e.g. waste-water treatment-plant effluent) and less obvious groundwater contributions. One of the simplest and most common conceptualizations of a stream (Figure 18.1(A)) shows a well-defined channel, with distinct inflows from tributaries, seeps and groundwater discharge pathways. In this conceptual view, a stream reach is either gaining or losing water, but never both simultaneously. A more complex and realistic view (Figure 18.1(B) and (C)) envisions an ill-defined channel with dispersed inflows from both surface and subsurface sources. In this conceptualization, a stream may be both gaining and losing water, possibly with hyporheic exchange flows (Bencala, 2005) returning water to the stream. The dispersed inflows to the stream may originate



**Figure 18.1** Conceptual diagrams of streamflow exchanges with groundwater in which (A) stream water sources are visible at the surface and (B) a more realistic conceptualization where, surface and subsurface sources as well as subsurface sinks may all exist in the same reach (e.g. within 100 m); and (C) a vertical cross-section conceptual model of stream–groundwater exchanges with associated locations of localized mixing noted. S indicates a seep, G indicates groundwater and T indicates tributary.

(Figure 18.2) on the hillslope ‘near’ the stream or at some greater distance further up-gradient from the stream. Further complexity (Figure 18.2) in the interpretation of solute sources arises due to the mixing of water in the riparian zone (Chanat and Hornberger, 2003).



**Figure 18.2** Conceptual model of stream-groundwater interactions representing proximate and distal flowpaths interacting with streams and proposing lateral flowpaths to streams mixing prior to directly interacting with streams.

The details of groundwater-stream connections may be significant to the discharge of water in large river systems (Konrad, 2006). In streams, the significance may most clearly be evident in the variability observed in the concentrations of solutes in inflowing waters. For example, in metal-rich streams that are either in relatively undisturbed catchments (Bencala *et al.*, 1990) or in highly impacted catchments (Kimball *et al.*, 2002), the magnitude of the signal of metal concentrations, from either groundwater seeps or tributaries, allows for variations in concentrations to be observed on the scale of tens of metres along streams.

## Processes

The spatial and temporal distributions of solute concentrations and loads (as the product of discharge and concentration) throughout stream networks are controlled by sources and the processes of transport, mixing and storage. Solute inputs to streams vary in time and space. Instantaneous, focused inputs or point sources are generally episodic and localized (e.g. the accidental spill of a solute at a particular location). Inputs of longer distributions can be both point sources, such as sewage outfalls, or more widely distributed, non-point sources, such as atmospheric deposition. Solutes may reach the stream network at the surface (e.g. spill) and via the subsurface (e.g. mineral weathering). Regardless of the source type, changes in stream-solute concentrations are not necessarily coincident with a change in solute load, as, for example, water entering streams with low solute concentrations will dilute stream concentrations, but increase stream discharge. Here, we discuss the processes of solute transport and fate, rather than sources in a watershed.

Four processes influence solute transport and solute load throughout a stream network: these are advection, dispersion, transient storage and the mixing of different

source waters. All solutes are subject to these physical processes. Additionally, non-conservative solutes are likely to be subject to chemical reactions and transformations. As such, the role of transient storage may be especially important because of the increased travel time either in surface dead zones, where photochemical reactions may occur, or in the subsurface, where solutes are in close contact with biofilms on sediment surfaces. Non-conservative solutes may also be influenced by mixing, if inflows introduce other mutually reactive solutes. We focus only on the conservative nature of solute transport throughout stream networks, and the potential for non-conservative transformations altered by or controlled by transient storage and mixing with inflows, in particular. Here, we introduce the four hydrologic processes, and then discuss the ways in which conditions throughout a stream network modify the magnitude of these processes and their consequential influence on stream-solute transport.

Advection is the bulk transport of a solute in the channel downstream. One approach to directly measure the advection of solutes is performing a stream-solute tracer experiment. In a pulse-stream tracer experiment within an advection-dominated transport regime (i.e. most streams of moderate or high gradient), the arrival of the highest concentrations of the solute at a downstream location indicates the timescale of advection between the points of injection and recovery. Advection is controlled by stream flow velocity, which is related to discharge, by longitudinal gradient and by channel roughness, which can be described by several metrics, including the Manning Equation. Thus, changes in channel morphology and discharge from headwaters to outlet will generally lead to increases in advection rates downstream (Leopold and Maddock, 1953; Jobson, 1996). However, the reach-scale variability in channel morphology, as well as the temporal changes in discharge, can lead to deviations from general trends on local-spatial and short-time scales.

Longitudinal dispersion is the hydrodynamic spreading of solute both ahead of and behind the centre of the solute pulse. Spatial variability in flow velocity across the width and depth of the channel drives hydrodynamic dispersion. Dispersion is present in even the simplest of channels because velocity gradients in the flow are created by friction at the channel boundaries. The spatial variability in the distribution of flow velocity increases as the channel complexity increases, so that it is expected that dispersion is positively correlated to increasing channel complexity. Furthermore, longitudinal dispersion is generally expected to increase with increasing discharge (Wallis and Manson, 2004), as complex turbulence structures develop within the water column. Thus, as a pulse of an injected tracer or spilled contaminant moves downstream, longitudinal dispersion tends to spread the solute out, leading to reduced peak concentrations, but an increased duration of exposure.

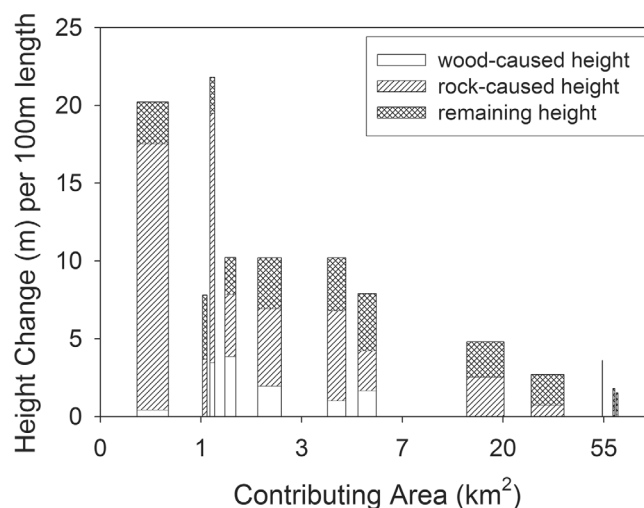
Transient storage is the movement of solute into and out of channel dead zones (side pools, eddies, slackwater etc.) or the subsurface, along hyporheic flowpaths. Transient storage slows the movement of water and solutes relative to that expected from advection and dispersion alone (Runkel, 2002). Typically, there is a wide range in the distribution

of transient-storage times within any given stream reach, ranging from small pools or eddies, that retain water for only a few seconds, to off-channel wetlands or long hyporheic flowpaths where stream water may be retained for days or weeks. In all cases, transient storage provides additional opportunities for non-conservative solutes in the stream water to contact surficial sediments or aquatic macrophytes. These surfaces are usually colonized by bacteria, fungi and algae, forming biofilms in which chemical and biological processes can transform many non-conservative solutes (Battin *et al.*, 2003). Hyporheic exchange flows are especially important in this regard because the stream water flows through the sediment filling the stream valleys, bringing solutes into intimate contact with sediment surfaces.

Channel roughness, as a function of bed material and morphology, has been shown to be an important control on hyporheic exchange (e.g. Bencala and Walters, 1983; Harvey and Bencala, 1993). At a small spatial scale ( $< 1 \text{ m}^2$ ), bed material and its arrangement control the local texture and shear between the water and bed. This influence of channel friction on the moving water affects advection and hydrodynamic dispersion. Also at these scales, Elliot and Brooks (1997) demonstrate that the pressure variation along sandy streambeds that were dominated by dune and ripple bedforms induces hyporheic exchange. Their 'pumping-exchange' model has been applied in various flume settings (see Packman and Bencala (2000) for a summary) and is likely to explain hyporheic exchange processes in most lowland sand-bed rivers. At the channel-unit scale, flow velocity is highly variable, with deeper, slower water in pools, compared to shallower and faster water in riffles, at low to moderate discharges. Because of the dynamics of channel hydraulics, an uneven hydraulic pressure distribution is realized across the streambed (longitudinally and laterally). Flowing water and subsurface water near the channel boundary react to these pressure differences, driving stream water into the bed at some locations (downwelling) and allowing subsurface water to flow into the surface channel at other locations (upwelling). The patterns of upwelling and downwelling locations are largely driven by breaks in the channel slope. Thus, the pattern of steps, pools and riffles will dictate exchange patterns (Anderson *et al.*, 2005; Gooseff *et al.*, 2006). Channel morphology is typically determined by the balance between sediment supply and transport capacity, which tend to vary. However, in some streams, inputs of large wood from adjacent forests can also control channel morphology (Figure 18.3).

The net effect of hyporheic exchange flows on solute transport depends on both physical and biogeochemical processes (Bencala, 2005). The physical controls are succinctly summarized by Darcy's Law:  $Q_{\text{HEF}} = -kA(\Delta H/\Delta L)$ , where:  $Q_{\text{HEF}}$  is the hyporheic exchange flow,  $k$  is the saturated hydraulic conductivity,  $A$  is the cross-sectional area through which flow occurs and  $\Delta H/\Delta L$  is the head gradient. Clearly, high-gradient streams with coarse-textured bed sediment (large  $k$ ) have a great potential for hyporheic exchange. Conversely, low-gradient streams flowing over fine-textured bed sediment have a much smaller potential for hyporheic exchange. It is important to consider the





**Figure 18.3** Change in elevation over 100 m of stream length for 12 reaches surveyed in the Lookout Creek basin, Oregon, a fifth-order catchment, as a result of general gradient, steps created by boulders and steps created by wood. The width of the bars is not indicative of any metric. Wood-caused steps have a maximum impact on bed height change around 1–2 km<sup>2</sup> contributing area, whereas headwater reaches (< 1 km<sup>2</sup> contributing area) have the greatest change in height due to rock-caused steps. Data from Anderson (2002).

amount of hyporheic exchange flow ( $Q_{\text{HEF}}$ ) that occurs over a given length of stream channel, relative to the stream discharge ( $Q$ ) flowing through that channel. In small, steep mountain streams ( $1.0 \text{ L/s} < Q < 10 \text{ L/s}$ ), hyporheic exchange flows at any given point in the channel can be large relative to the total stream discharge, such that the entire surface stream flow is cycled through the hyporheic zone over distances of less than 100 m (Kasahara and Wondzell, 2003; Wondzell, 2006). As streams increase in size,  $Q$  increases more rapidly than does  $Q_{\text{HEF}}$ , so that in larger mountain streams and rivers the amount of hyporheic exchange flow is usually small relative to the total stream discharge, and turnover lengths are very long. From the point of view of simple mass transport, then, the hyporheic zone can have a substantial effect on solute transport in small headwater streams with generally rough channels but is unlikely to have a substantial effect on solute transformations in low-gradient streams with fine-textured bed sediment or in larger streams and rivers.

The net effect of hyporheic exchange flows on water quality also depends on both the rates of biogeochemical processes and the stream-water residence time in the hyporheic zone (Gooseff *et al.*, 2003, Figure 7). Hyporheic exchange flows in small, steep mountain streams tend to have short residence times because flowpaths are relatively short, head gradients steep and hydraulic conductivities large. In contrast, moderate-gradient, larger streams flowing through wide, mountain stream valleys provide opportunities



for long flowpaths with long residence times (Kasahara and Wondzell, 2003). In both cases studied by Kasahara and Wondzell (2003) of low-order and mid-order reaches, hyporheic residence time distributions were highly skewed, with two- to four-hour residence time dominant, but median residence times were only 18 hours in the small stream and 27 hours in the large stream. In both streams, flowpaths with a residence time of 20 or more days were present (Kasahara and Wondzell, 2003). The relative importance of the residence time and quantity of hyporheic exchange in controlling the flux of non-conservative solutes in stream networks has yet to be determined, though it varies along the channel network, in response to changes in corroborating factors (e.g. fluvial geomorphology) from headwaters to larger-order streams.

The potential influence of the hyporheic zone on contaminants moving down the stream network is complex because of the variety of environmental conditions found throughout the hyporheic zone, the variety of chemical and biological reactions that can occur there and the wide variety of the types of possible contaminants. While we cannot explore these issues in depth, there are several generalizations that should be considered. First, because hyporheic exchange significantly retards the transport of some portion of solutes moving through the channel, hyporheic return flows could potentially extend the period of exposure to, or the total watershed residence time of, a contaminant from an accidental spill. Contaminant concentrations will be low in the extended late-time tail of the contaminant plume, however, so that this would present a concern only for contaminants that pose a water-quality threat in low concentrations. Alternatively, the hyporheic zone could store large amounts of contaminants introduced from long duration inputs. In this case, long periods may be necessary to realize the benefits of eliminating sources. Secondly, if contaminants entering the hyporheic zone are highly reactive, it is possible that they could be bound to sediment or organic particles and removed from downstream transport. Eventually, however, erosion is likely to liberate contaminated sediment, which may pose problems at some later time. Alternatively, a variety of contaminants will be transformed by biogeochemical processes in the hyporheic zone. For example, where nitrate is transported to anoxic locations, it can be permanently removed from a solution by denitrification (Peterson *et al.*, 2001).

Lateral inflows and outflows can alter stream-solute loads, depending on solute concentrations in inflowing water. There are a number of studies that document solute and water inflow to streams, particularly in the interest of headwater contributions of diffuse any metal-rich drainage to streams (e.g. Bencala *et al.*, 1990; Kimball *et al.*, 2002). There are also some studies documenting streamflow losses throughout watersheds, primarily reporting the results of seepage meter runs (several distributed points of discharge measurement throughout the stream network) (e.g. Konrad, 2006; Laenen and Risley, 1997; Ruehl *et al.*, 2006; Zellweger, 1994). Such methods do not account for reach-scale gross gains and losses of water, considering only the net gain or loss (as the difference between gross gains and losses) between measurement locations. Hence, reach-scale gains and losses of solute are generally derived from net changes throughout the stream

network. The likelihood of a complex pattern of gross streamflow gains and losses along streams (Payn *et al.*, 2005) suggests that there is a coincident complex pattern of solute mixing with inflows along stream networks.

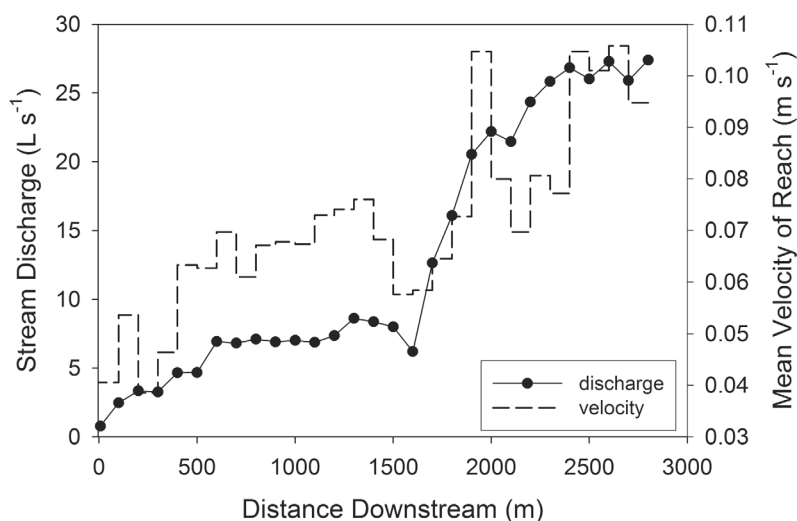
All four of these processes (advection, dispersion, transient storage and mixing) are reasonably easy to investigate in reach-scale stream experiments but are much more difficult to study at the scale of the entire stream network. We know, however, that these processes affect solute transport at the reach scale. Therefore, we expect the combined influence of these processes on solute transport to be manifest in the cumulative stream network signal. The cumulative effects are not strictly additive, particularly in the cases of hyporheic exchange or streamflow gains and losses, both of which may potentially operate over significant spatial scales to link shorter reaches. We are currently limited if we want to develop field experiments or empirically analyse solute transport through entire stream networks. Transient storage and mixing processes are especially problematic because hyporheic exchange and groundwater inflows are heterogeneous in both time and space. Furthermore, because they are greatly influenced by subsurface processes, they are difficult to measure. For example, the practice of sampling only tributaries and visible surface seeps will ‘miss’ solute inflows deep beneath the stream from distal sources in the catchment (Figure 18.1(C)), and yet it is not feasible to sample truly representative groundwater without expensive equipment, which is not necessarily available to all. Furthermore, the field characterization of mixing with inflows and transient storage is limited by the resolution of tracer analyses (Harvey and Wagner, 2000), tracer-concentration analytical limitations and the properties of current tracers.

## Linking transport processes with the fluvial geomorphic template

### Network controls on solute-transport processes

Examining solute transport within whole networks presents substantive challenges. Although transport is controlled by advection, dispersion, transient storage and mixing with inflows, it is difficult to quantify any of these at the scale of an entire watershed. Therefore, we examine higher-order controls on physical transport. These are: discharge, channel form (geomorphology and network topology) and near-stream hydraulic gradients. These controls vary spatially throughout a watershed and at different temporal scales as well. Discharge is the primary control on solute transport in the channel, affecting advection and dispersion processes through hydraulic characteristics, as well as bulk dilution for solute mass. The relationship between discharge and flow velocity (Leopold and Maddock, 1953) is critically important, showing that transport times will be much faster at higher discharges. In humid areas, discharge is usually proportional to drainage

area so that, in conventional characterizations, stream discharge and transport velocity increase downstream. This pattern may not hold in arid regions, however, where stream losses to evaporation or aquifer recharge may lead to a diminishing discharge with accumulated drainage area. Even in humid regions, discharge does not increase smoothly with accumulated drainage area or distance from source. For example, in a  $\sim 2$ -km section of a second-order stream in Montana, we characterized stream discharge and advection by synoptically releasing salt-slug tracers approximately every 100 m. The results (Figure 18.4) show a spatially inconsistent increase in discharge and associated velocity, including some locations where discharge and velocity both decreased. Similar dynamics have been observed in the main stem of the Willamette River in Oregon, USA (Laenen and Risley, 1997, Figure 14), suggesting that such patterns are likely present in many larger rivers as well.



**Figure 18.4** Spatial distribution of flow velocity and discharge measured with salt-tracer injections in consecutive 100-m reaches in a second-order watershed in Montana (RA Payn, unpublished data).

The simple metrics of channel shape often exhibit characteristic patterns in relation to either basin area or discharge. Early work by Leopold and Maddock (1953) showed that both channel width and depth increase with increasing annual average discharge (see also Saco and Kumar, Chapter 15, this volume). The combination of discharge and channel morphology – especially the downstream increases in discharge, width and depth – have important implications for contaminant transport. In general, small streams will be much more retentive than large rivers, but this is not just a consequence of increasing the flow velocity. The water-sediment interface is a highly reactive surface for some solutes (e.g. metals, nutrients, dissolved organic carbon, hormones etc.). In small streams, the size of the wetted streambed area is high relative to discharge, and

water depths are relatively shallow, allowing for a substantial interaction between solutes in the water column and the streambed (Peterson *et al.*, 2001). The situation is reversed in large rivers where flow velocities tend to be much higher, water depths greater and the wetted streambed area is small relative to discharge, all of which combine to limit solute retention. Table 18.1 demonstrates these relationships for the 64 km<sup>2</sup> Lookout Creek watershed in central Oregon. The reduction in the ratio of wetted perimeter to annual mean  $Q$  at higher stream orders indicates a restriction for hyporheic exchange, compared to low-order reaches. Rivers with large quantities of aquatic macrophytes might be an exception to this general trend, as the stems and leafs provide large surface areas that are also colonized by biofilms and can add substantial roughness to the channel so that they also slow water velocity (Ovesen, 2001), making the river more retentive than would otherwise be expected.

**Table 18.1** Summary network characteristics for the fifth-order Lookout Creek catchment in central Oregon, USA, where  $Q$  is the mean annual discharge and 'Area' refers to the total catchment area contributing to reaches in each stream order, throughout the basin. Data from Wondzell (1994).

Stream Order	Total Network Length (%)	Area (%)	$Q$ (m <sup>3</sup> s <sup>-1</sup> )	Wetted Perimeter $P$ (m)	$P/Q$
1	53	66	0.005	2.36	487.60
2	23	16	0.026	4.36	167.37
3	13	10	0.369	8.34	22.59
4	5	4	1.558	12.10	7.77
5	6	4	3.256	15.30	4.70

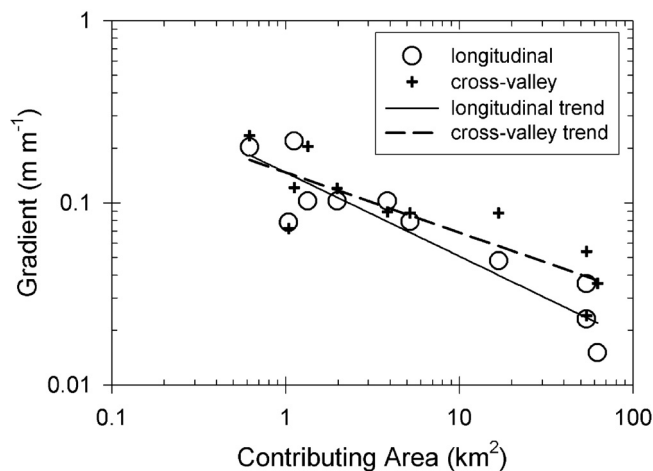
Hyporheic exchange flows also are an important determinant of solute retention, as described above. Substantial research has shown that exchange flows are strongly controlled by channel morphology (the shape of the channel and the valley floor) (see Wondzell (2006) for more detailed discussion). In turn, channel morphology often shows characteristic patterns in relation to either basin area or discharge (Montgomery and Buffington, 1997, Figures 4 and 5). Detailed morphologic studies have shown that channel morphology broadly results from the balance between sediment supply and transport capacity (Montgomery and Buffington, 1998). Within areas with reasonably similar bedrock lithology, climate and topographic relief, both sediment supply and transport capacity will follow characteristic patterns so that reach slope, channel constraint (the width of the channel relative to the width of the floodplain) and watershed area will be the primary determinants of channel morphology (Chartrand and Whiting, 2000; Montgomery and Buffington, 1998).

The consequence of systematic changes in channel morphology on a gradient of increasing stream size is an increase in median hyporheic residence time and a concurrent

decrease in the amount of hyporheic exchange flow, relative to stream discharge, as drainage area accumulates (Kasahara and Wondzell, 2003). Data collected from small mountain streams in the fifth-order Lookout Creek basin showed that variation in the longitudinal profile of the stream channel (steps or riffles) was a primary driver of hyporheic exchange flow (Kasahara and Wondzell, 2003; Anderson *et al.*, 2005). Steep head gradients around abrupt changes in channel elevation, such as steps, tend to drive abundant exchange flows, but both flowpath length and residence times tend to be short. The prevalence of steps changes systematically through the stream network, accounting for 80 per cent, or more, of the elevation change along headwater streams, but only 50 per cent in mid-order streams (Figure 18.3). While mountain streams of all sizes show lateral complexity as measured by channel sinuosity and the presence of secondary channels, these features tend to be poorly developed in small headwater streams and increasingly better developed as the stream size increases and longitudinal gradients weaken. The actual expression is, however, controlled by channel constraint. Narrow valley floors, constrained by bedrock or other factors, leave little room for streams to develop lateral complexity. Conversely, in wide alluvial valleys, channels are often complex and support relatively large hyporheic exchange flows between main and secondary channels (Kasahara and Wondzell, 2003) driven by increasingly steep lateral head gradients (Figure 18.5). We know of no similar systematic, network-scale analysis of the geomorphic factors driving hyporheic exchange flows in either foothill or lowland rivers. Therefore, we do not know if the trends observed in mountain-river networks can be extended to river networks in other geomorphologic settings.

To demonstrate some of these temporal and spatial changes in solute transport, we present data from repeated stream-tracer experiments in Stringer Creek, a second-order mountain stream in the Little Belt Mountains of Montana (Figure 18.6). We conducted slug injections of Rhodamine-WT (RWT) at the head of the reach in June and July and monitored RWT breakthrough curves (BTCs) at the upper (1660 m downstream) and lower (1408 m further downstream) stream gauges. Discharge was too low in August to perform additional injections above the upper gauge. A third slug injection was performed from the upper stream gauge to lower stream gauge in early September (Figure 18.6(B)). As stream discharge receded throughout the summer, advection decreased substantially (as indicated by the later arrivals of peak concentrations), and dispersion increased (indicated as the spread of the arriving 'hump' of the BTCs), and apparent transient storage increased (as indicated by the total lengths of the BTCs), in both sections of the stream (Figures 18.6(C) and 18.6(D)). The third injection in the lower reach shows evidence of further decreasing advection, but dispersion and transient storage comparisons are not valid because the tracer was released at the upper gauge rather than the stream head.

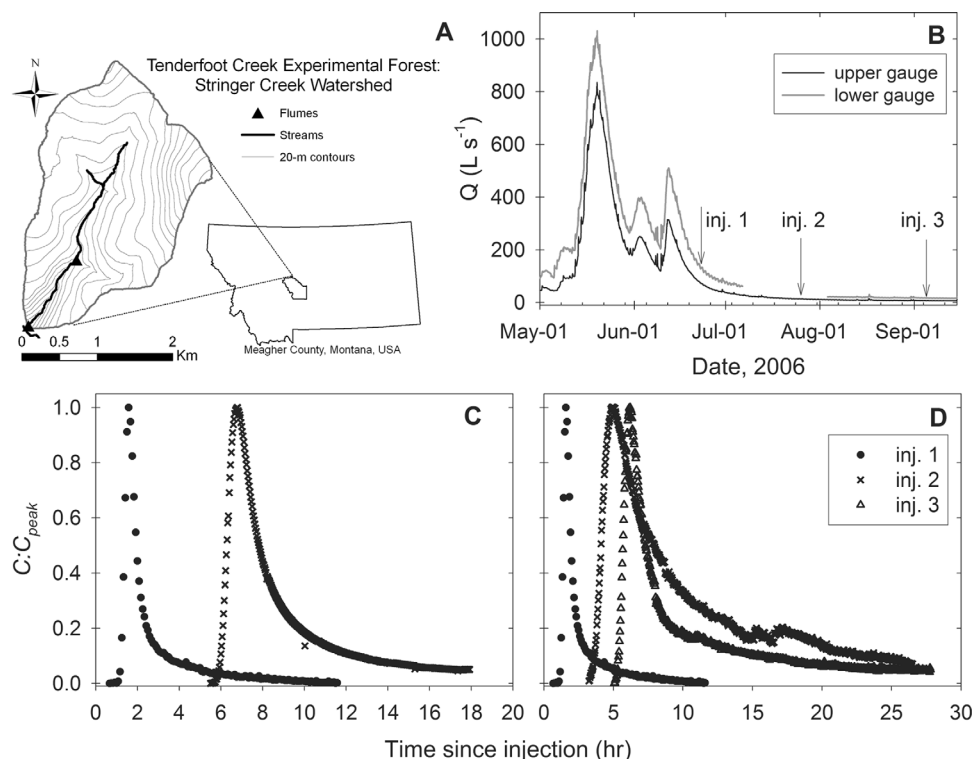
Whereas large-scale patterns in discharge, flow velocity and channel shape influence general network-scale trends, reach-scale variability in channel morphology can lead to a substantial departure from expected trends. Especially important in mountain stream



**Figure 18.5** Longitudinal topographic gradients along the thalweg of the stream, and cross-valley gradients in water-surface elevation measured normal to stream flow direction, as surveyed in 10 reaches throughout the Lookout Creek basin, Oregon, USA. Note the tendency for cross-valley gradients to increase, relative to longitudinal gradients, with increased drainage area. Data from Anderson (2002).

networks are wide alluvial valleys whose presence can be controlled by large-scale geologic factors, such as faulting patterns and bedrock contact, by past patterns of glaciation and also by sediment deposition from tributary channels. Stream confluences are often hotspots (locations of enhanced activity) of biological and chemical activity (Fisher *et al.*, 2004; Rice *et al.*, Chapter 11, this volume), driven in part by the complexity of environments found in these locations. In large mountain rivers, confluences often mark major knickpoints in the longitudinal gradient, caused by the deposition of sediment transported into the main-stem channels by tributaries during major floods or by debris flows (Benda *et al.*, 2003). Large boulders tend to dam the main channel, leading to a subsequent deposition upstream of the confluence, building wide, complex valley floors. Such valley-floor environments, with multiple channels and increased sinuosity, have been shown to be important locations for hyporheic exchange flow (Kasahara and Wondzell, 2003).

The general trends in discharge and channel shape and morphology with increasing basin area discussed so far ignore anthropogenic effects on river networks. Throughout the world, river networks have been reshaped by humans (Gregory, 2006), changes that have potentially large effects on solute transport. Obviously, large impoundments will dramatically slow network transport times (Vitousek *et al.*, 1997). Conversely, channelization and dike construction have dramatically simplified some rivers (Sedell and Froggatt, 1984; Triska, 1984), and the resulting straightened and narrowed channels should have much faster transport times. The associated losses of side channels and other lateral complexity combined with increased fine-sediment inputs are also likely



**Figure 18.6** Stream-tracer dynamics in Stringer Creek, Montana in 2006; map of study site (A), hydrograph for the upper and lower gauges on Stringer Creek (B), and Rhodamine WT breakthrough curves at the upper gauge, 1660 m downstream of injection point for injections 1 and 2, which was the eastern stream head (C), and the lower stream gauge, 1408 m downstream of the upper gauge. Injections 1 and 2 were performed on 23 June and 26 July respectively. A third injection was performed on 5 September, starting at the upper gauge. Travel times in panel (D) represent travel from the upper gauge to the lower gauge, to facilitate the comparison of times to peak concentration. Some discharge data from the lower gauge is missing in panel (B), owing to equipment failure.

to restrict hyporheic exchange flows. In many intensively farmed landscapes, the entire drainage network, from buried field drains and the smallest headwater channels to the largest rivers, have been modified to speed the movement of water off the landscape. Water and solute retention is poor in such networks. In large river settings, floodplains can be important locations of solute processing (particularly nutrients) (Mitsch *et al.*, 2005). However, the propensity to create flood-control structures, such as levees, disconnects rivers from their floodplains (Mitsch *et al.*, 2001).

From a simple mixing-model approach, the mixing of stream waters at tributaries or with inflowing groundwater causes a change in solute load, the product of discharge and solute concentration. The spatial distribution of solute loads throughout a stream net-



work at any moment is dictated by the balance of distributed lateral loads to the stream. Dilute lateral inflows of water to streams from groundwater (assuming conservative mixing) will not change loads of a particular stream solute because the mixing of these waters in the channel will increase discharge and proportionally decrease channel solute concentration. However, solute-rich inflows, such as metal loads from acid mine/rock drainage, will increase stream loads of those constituents, until chemical reactions take place to reduce their stream loads. Temporal trends of solute loads at any one point in a channel network are driven by changes in channel discharge and the associated upstream inputs of water and solute.

Temporal changes in discharge, be they seasonal, event responses or diurnal, will affect processes that control solute transport in stream networks. At high-flow conditions, advection and dispersion will increase, but transient storage will diminish because of fewer in-channel dead zones, and because of the reduced relative hyporheic exchange (i.e. in proportion to total discharge). The reduction in the relative hyporheic exchange flow to channel discharge lessens at high-flow conditions because the effect of channel morphology on the energy grade line is dampened and more continuous, thus reducing the local head gradients that drive hyporheic exchange. However, hydraulic conductivity of the bed does not necessarily change from high- to low-flow conditions. Therefore, a reduction in head gradient and a consistency in hydraulic conductivity will result in reduced hyporheic exchange flows. Solute transport is generally enhanced through stream networks at high flow because there is less buffering capacity of the network to retard solute transport.

## Forward-looking perspective

There are several perspectives in which we can advance our understanding and analysis of solute transport along stream and river networks. The process of solute transport along stream and river networks is by-definition integrative. Three fundamental questions from physical hydrology control this transport: (1) 'Where does the water moving to a stream come from?', (2) 'How long does it stay in the channel?' and (3) 'How long does it take to get (back) into the channel?'. Although these questions have been partially answered, we know of no synthetic study that examines these three questions within a large river network and examines how such relations change with time and with location. Answering these questions at a network scale remains a challenge for understanding hydrologic processes, distributed stream-solute loading and solute transport.

## Concepts

Three directions are apparent for advancing a process-based interpretation of solute loading to, and transport along, river networks. The stream does not stand alone,

rather it is intimately connected to its catchment, often in ways that are not easily visible. As such, spatially and temporally distributed mixing processes influence solute concentration, and at any one point the solute signal is an integration of upstream mixing processes and concurrent transport processes in the stream channel.

### **Stream–catchment connections**

The significance of the components of inflow and exchange shift spatially with distance downstream through the catchment, and temporally in response to catchment flow periods. In the upland reaches a stream will gain, and lose, water in visible and relatively shallow flow systems of dispersed seeps and springs. Further downstream spatially distributed connections between the stream and groundwater flow systems will develop. As the network of streams and rivers develops, changes in flow where tributaries meet effectively become point sources. As these changes in water inflow sources occur, there will be changes in stream-solute loads throughout the stream network.

### **Mixing of inflows and hyporheic flows**

Mixing through the riparian zone and along hyporheic exchange flowpaths brings further complexity to the identification of ‘true’ inflow (Cox *et al.*, 2003; Hinkle *et al.*, 2001). This mixing among distal, near-stream and stream waters (Figure 18.2) complicates our notion of end-member contributions to streams, as end-member hillslope, groundwater and stream waters are masked by the mixing process prior to reaching the stream network.

### **Integration within the stream channel**

Catchment, near-stream and in-stream characteristics all are significant in determining the fate of solutes entering the stream channel. As the network of streams and rivers develops, the downstream reaches are necessarily integrations of upstream and up-valley characteristics and processes. However, within this integration, the downstream-solute concentrations are not necessarily the well-mixed sum of the inputs. The relative roles of in-stream biogeochemical and physical processes will vary.

### **Analysis tools**

The progress made in conceptual understanding needs to be realized in the quantitative descriptions of solute fate. The advection–dispersion transport equation has long been

the standard tool for the analysis of solute transport in streams and rivers. Particularly applicable in upland streams, the transient storage model has been useful in drawing our attention to the significance of catchment-stream and hyporheic connections. At the beginning of this century, several modelling approaches are being developed and applied, which further our abilities to quantify transport processes.

Simulations of solute transport using general residence time distribution models (Haggerty *et al.*, 2002; Gooseff *et al.*, 2003) enable the identification of the timescales of exchange, particularly along hyporheic flowpaths, which are varied and possibly quite long compared to in-stream transport.

At the process level, the methods of environmental fluid mechanics (e.g. Ren and Packman, 2004; Marion *et al.*, 2002; Cardenas *et al.*, 2004) are quite successful in interpreting solute transport in flumes. The future challenge is to bring these models and results to field situations. The complexities of flow at the stream–catchment interface have been well simulated (e.g. Kasahara and Wondzell, 2003; Lautz and Siegel, 2006) using the MODFLOW representation of groundwater flow. This approach has required appreciable investments in monitoring the physical systems over relatively small areas. The application of groundwater-flow modelling to define hyporheic flowpaths (e.g. Gooseff *et al.*, 2006) requires refinements in the characterization of the spatial variability of subsurface hydraulic conductivity and the representation of stream-boundary conditions (Tonina and Buffington, 2007).

Models are only one set of analytical tools which need development to transfer our knowledge and approaches from individual streams to networks. In part, the reason that we have made significant advances in understanding discrete reach-scale solute transport and fate, but not moved to larger spatial scales, is that the spatial scale of the reach and the corresponding timescales of processes are most appropriate for the current stream tracer methodology (Harvey and Wagner, 2000; Gooseff *et al.*, 2005). However, these experimental approaches are constrained by analytical limits of tracer-concentration measurement and the properties of the tracers currently available. Thus, there is a clear need to develop and apply more robust conservative hydrologic tracers, detectable at very low concentrations.

## Field studies

There is no one measurement approach for identifying the inflow of water and solutes as the connections of a stream to its catchment shifts. Rather, the challenge to our thinking and our practice is to be aware of the spatially changing nature of these connections. Field observations of the actual paths are needed, and may be facilitated by the application of geophysical field methods to studies of the transport of stream solute. New techniques that corroborate geophysical measurements with hydrologic techniques will in the future provide the spatial data needed to expand this mod-

elling effort to longer stream reaches. Challenges in incorporating connections to the catchment include the matching of detailed field studies to the in-stream modelling of solute transport to develop a better understanding of the effects of channel evolution (Harvey *et al.*, 2003), the characterizations of transport most significant to solute dynamics (Runkel, 2002), and scaling up our process-understanding of river systems (Fernald *et al.*, 2001).

Ultimately, our understanding of solute transport and fate at the scale of river networks will be advanced by developing new conceptual models, testing those models through the acquisition of field data and subsequently developing new numerical models to characterize solute transport in river networks. This process will be iterative as, for example, new advances in field methods may better inform further refined conceptual or numerical models. The succinct characterization of solute transport through river networks remains a challenge for environmental scientists, though the recent advancements in conceptual framework, modelling and field studies point to significant advances in the coming years.

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