Predicting changes in hydrologic retention in an evolving semi-arid alluvial stream

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Abstract

Hydrologic retention of solutes in hyporheic zones or other slowly moving waters of natural channels is thought to be a significant control on biogeochemical cycling and ecology of streams. To learn more about factors affecting hydrologic retention, we repeated stream-tracer injections for 5 years in a semi-arid alluvial stream (Pinal Creek, Ariz.) during a period when streamflow was decreasing, channel width increasing, and coverage of aquatic macrophytes expanding. Average stream velocity at Pinal Creek decreased from 0.8 to 0.2 m/s, average stream depth decreased from 0.09 to 0.04 m, and average channel width expanded from 3 to 13 m. Modeling of tracer experiments indicated that the hydrologic retention factor ($R_h$), a measure of the average time that solute spends in storage per unit length of downstream transport, increased from 0.02 to 8 s/m. At the same time the ratio of cross-sectional area of storage zones to main channel cross-sectional area ($A_s/A$) increased from 0.2 to 0.8 m 2/m2, and average water residence time in storage zones ($t_s$) increased from 5 to 24 min. Compared with published data from four other streams in the US, Pinal Creek experienced the greatest change in hydrologic retention for a given change in streamflow. The other streams differed from Pinal Creek in that they experienced a change in streamflow between tracer experiments without substantial geomorphic or vegetative adjustments. As a result, a regression of hydrologic retention on streamflow developed for the other streams underpredicted the measured increases in hydrologic retention at Pinal Creek. The increase in hydrologic retention at Pinal Creek was more accurately predicted when measurements of the Darcy–Weisbach friction factor were used (either alone or in addition to streamflow) as a predictor variable. We conclude that relatively simple measurements of channel friction are useful for predicting the response of hydrologic retention in streams to major adjustments in channel morphology as well as changes in streamflow.

1. Introduction

Understanding the linkages between stream ecology, biogeochemistry, and hydrologic transport has advanced appreciably over the past few decades through the use of stream-tracer injections [12,23]. Yet little is known about how hydrologic retention is affected by adjustments in streamflow or features of the channel such as channel aspect ratio, sediment type, roughness features, and presence of aquatic vegetation. Solute-tracer injections in streams provide precise reach-averaged estimates of stream velocities. In addition they have allowed researchers to estimate some characteristics of mixing that affect downstream transport, such as hydrologic storage [2]. ‘Storage’ refers to the temporary delay in downstream movement of water and solutes that results from water exchange between the active channel and slowly moving water at channel sides, at the bottom of pools, or in the streambed (hyporheic zone). A closely related concept is ‘hydrologic retention’, the average time that solutes spend in storage per unit length of downstream transport. Storage increases the contact area with biologically and geochemically active surfaces, such as periphyton biofilms or geochemical coatings on sediment. Hydrologic retention of solutes in storage zones creates more contact time for reactions to proceed for a given distance of downstream transport. To quantify storage and hydrologic retention, model...
simulations of the tracer experiments integrate the cumulative effects of small-scale processes at the scale of a stream reach. From these measurements and simulations, further models are developed for coupled flow, transport, and biogeochemical reactions in stream reaches (hundreds of meters to kilometers). In this regard hydrologic retention has become a key part of our understanding of how hydrology influences ecology of lotic ecosystems [18,24].

Tracer-derived measures of solute storage and hydrologic retention in streams were recently summarized [10,21]. Storage-zone area, $A_s$, and storage-zone water residence time, $t_r$, are the key reach-averaged measures of the storage process itself, whereas the hydrologic retention factor, $R_h$, is an integrated measure of the effect that storage has in delaying downstream transport of solutes. Tracer-derived estimates of these measures of storage have the desirable characteristic of averaging over small-scale variability in streams, which provides an appropriate basis for reach-scale and basin-scale modeling of solute transport. At the same time, these empirically derived estimates have a distinct disadvantage in not being transferable to other stream reaches or even to the same reach under different flow conditions [10]. As a consequence, it has been difficult for researchers to anticipate how storage processes will evolve given a change in streamflow or a change in physical characteristics in a stream of interest.

The goal of the present study was to determine how hydrologic retention changed as a result of adjustments in streamflow and geomorphic and vegetative characteristics in Pinal Creek, a semi-arid alluvial stream in Arizona. A second goal was to compare results from Pinal Creek with published data from other streams in an attempt to improve predictions of hydrologic retention for any channel where prior information about streamflow and simple channel characteristics is available.

While interactions between groundwater and surface water have been widely investigated [28], there have been fewer studies focused specifically on the physical controls on solute storage [10,19]. Wondzell and Swanson [30] recently investigated how subsurface flow paths through alluvium were affected by geomorphic changes in the channel and on the floodplain. Their investigation mainly documented changes in the direction of subsurface flow paths in the alluvium surrounding the channel. An alternative approach to detecting changes in storage zones is to conduct before and after tracer experimentation. One advantage of the tracer-based approach is that it provides a more direct measure of how storage affects the instream transport of solutes. Also, since many similar tracer studies have been conducted in channels all over the world, results can be widely compared. There are a number of other published investigations where storage processes were characterized on the basis of repeat tracer experiments in channels [3,7,9,14,15]. For example, Hart et al. [7] compared storage in temperate forested streams before and after leaf fall, and Morrice et al. [15] compared storage in a first-order mountain stream over changing flow conditions. Another approach was to conduct tracer experiments in paired experiment channels with different periphyton biomasses [17], or paired natural channels where some of the adjacent riparian zones had been heavily grazed and stream bottom characteristics affected by cattle crossings [16]. Repeat tracer experiments in natural channels generally have shown that storage-zone size and average water residence time in storage zones increased with decreasing streamflow [9,14,15].

Work by Morrice et al. [15] found that hydrologic retention decreased with increasing streamflow in a first-order mountain channel in New Mexico. While streamflow does explain some of the variability in hydrologic retention, this approach ignores the potential influence of changes in geomorphic and vegetative characteristics of the channel. Here we test whether changes in channel frictional resistance are a better predictor of how hydrologic retention responds to streamflow and channel change. Friction plays a direct role in creating zones of stagnant or recirculating water in the channel that temporarily store solute. Friction also increases the uneven pressures on the streambed that are the driving force for movement of stream solutes across the bed and temporary storage in subsurface (hyporheic) flow paths [19]. As a result we expected that friction was related to storage-zone size and water residence time, and thus might be a good predictor of hydrologic retention, especially in streams that differ in their channel physical features or experience a change in channel physical features over time. Other factors that are known to be important in driving channel changes in southwest alluvial basins include climate variability [4], groundwater recharge, discharge, and evapotranspiration [22,32], cattle grazing [16], and feedbacks between sediment transport, channel vegetation, and channel frictional resistance [5,6,13,27]. Fig. 1 summarizes the inter-relationships between variables affecting hydrologic retention in channels of semi-arid alluvial basins. Most of the driving forces for channel change that are indicated in Fig. 1 were operative at one time or another during the 1990s in Pinal Creek basin. In the mid to late 1990s, Pinal Creek rapidly underwent a transformation from a fast-flowing alluvial stream to a slowly flowing wetland stream. Our tracer studies conducted during the mid and latter 1990s documented how those changes affected hydrologic retention. Using additional published data from other US streams, we developed predictive relationships that demonstrated the importance of simple measures of channel friction as a master variable that can resolve how a wide variety of very different channel changes will affect hydrologic reten-
tion. The practical outcome of the work is a two-predictor regression equation based on simply measured variables that is useful for estimating hydrologic retention in any stream.

2. Study site

Pinal Creek is a high-gradient (1%) perennial desert stream draining an alluvial aquifer in east-central Arizona (Fig. 2). Frequent floods and abundant sediment supply in Pinal Creek basin created a broad alluvial floodplain that, in the 1980s and early 1990s, was composed of coarse sand, gravel, pebbles, and cobbles with little riparian vegetation. The channel planform was straight or gently meandering between terrace edges, generally not incised, with braiding in some areas and infrequent pools and riffles. The gravel bed of the channel had an average slope of 0.01 and a median grain size of 2 mm for bed material smaller than cobbles. The streambed and bank sediments had minimal fine material, organic matter, or extensive root systems. Riparian vegetation consisted mainly of tamarisk seedlings on the alluvial floodplain, with willows and a few mature cottonwoods on the lower terraces farther from the channel. Mesquite was (and still is) the dominant tree on the higher and older parts of the terraces. Due to clearing of most of the large cottonwoods decades ago, the channel was not shaded significantly. Frequent floods and grazing and trampling by cattle kept the coverage of aquatic and riparian herbaceous vegetation to a minimum prior to the mid 1990s.

Streamflow in Pinal Creek fluctuates due to natural climatic cycles and human uses (i.e. groundwater pumping). In the past 20 years pumping of groundwater has increased to remediate an accidental release of waste solutions to groundwater from ore processing facilities. Streamflow and channel form at Pinal Creek were also affected in the latter 1990s by a decrease in the occurrence of floods. Based on 16 years of record, Pinal Creek floods occurred more frequently in the early 1990s than in the late 1990s. A major flood (>3000 cfs) occurred in 1993 during a rain on snow event in January that produced floods of record across much of Arizona. That flood also caused significant recharge to the alluvial aquifer in Pinal Creek basin, raising by approximately 20% the baseflow in the stream after the flood had subsided (Fig. 3). Another large discharge (360 cfs) occurred in January 1995. Following that there were no floods of any significant magnitude for 32 months until a summer monsoon created a small flood (27 cfs) in August of 1997. Small to moderate floods (30–100 cfs) have continued at a rate of once or twice per year since August 1997 (Fig. 3).

Beginning in 1996 there was a proliferation of aquatic and riparian vegetation (Fig. 4) that we believe resulted, in part, from the decreased occurrence of floods. Also important may have been the transport of new sediment into the perennial reach that had been mobilized by the flood from upstream areas of the channel that are normally dry. Human re-engineering of the perennial channel in its uppermost reaches for several years following the 1993 flood probably also played a part in mobilizing new sediment. We include in Fig. 3 a notation about the increasing rate of groundwater pumping in the lower basin (beginning in 1999), because it definitely lowered streamflow during the 1999 tracer experiment and may have influenced the eventual trajectory of channel changes in Pinal Creek. However, the increased groundwater pumping began too late to explain the initial period of proliferation of vegetation and widening of the channel in the mid 1990s. Like
groundwater pumping, removal of cattle from the experimental reach also may have played a role in channel change, due to the decreased effects of trampling of aquatic vegetation and grazing on incipient riparian vegetation. However, that change also probably occurred too late (beginning gradually in 1997 until complete removal of cattle in April 2000) to explain the initial rapid expansion of aquatic vegetation in 1996 and 1997.

Expanding coverage of riparian vegetation began with the spread and persistence (i.e. over wintering) of aquatic vegetation in 1996 and 1997, followed by the establishment and growth of emergent macrophytes and riparian shrubs and trees close to the channel. During the period 1996–1999 the channel cross-section widened and shallowed, and streamflow velocity slowed due to the increased frictional resistance of aquatic vegetation. The change in channel form from a fast-flowing stream to a slow-flowing wetland stream appears to be significant enough that channel response to more recent floods has been affected. Floods in the early 1990s commonly removed aquatic vegetation. For example, we observed that a flood of 80 cfs in the summer of 1994 swept the channel mostly clean of aquatic macrophytes. Yet floods over 100 cfs in the latter 1990s had little effect on aquatic macrophytes. The well-established vegetation in the current channel system appears to be more resilient to floods.

3. Methods

Stream tracer tests were conducted annually from 1994 to 1999 (excluding 1996) along a subreach of Pinal Creek (Fig. 2). Each tracer test consisted of a constant-rate injection of KBr (potassium bromide) for 3 h or longer at a location that promoted complete vertical and horizontal mixing across the stream by the time tracer had reached the upstream end of the study reach. Sampling for the tracer was conducted at both the upstream and downstream ends of the reach. A second,
shorter (1–2 h) injection was conducted (on the prior or subsequent day) at the downstream end of the reach, in order to provide the additional data needed to estimate groundwater exchange.

All tracer tests were conducted in the same general subreach of Pinal Creek, approximately 2-km upstream of the USGS continuous gaging station at Inspiration Dam (Fig. 2). Because the gage is located further downstream, it records a value that is typically several cfs higher than results from the experimental subreach. However, the same general pattern of decreasing baseflow between 1994 and 1999 is evident from both streamflow records (Fig. 3 and Table 1). The endpoints of the experimental subreach varied each year, for several reasons, beginning with the need to locate the injection at a point where natural channel features would promote rapid vertical and cross-channel mixing. The location of the downstream endpoint of the experimental subreach was also shifted each year. This was necessary to improve the reliability of tracer-determined parameters on the basis of experimental design principles and preliminary estimates of flow and transport conditions [26]. The suggested procedure is to obtain preliminary estimates of a few key transport parameters, usually by making some simple preliminary measurements in the intended study reach. The next step is to use a theoretical analysis based on the Dahmkohler number to compute the optimal reach length for the detailed tracer experiment, i.e. the reach length that is most likely to minimize uncertainty of the parameters that are to be determined by modeling [10]. For our study this approach resulted in shorter reach lengths in later years. Consequently, more effort was required each year to select new subreach endpoints that were as representative as possible of channel conditions along the boundaries of the original 1-km reach. The overall changes in channel form and flow velocity at Pinal Creek were significant enough over time that it is likely that the effect of minor adjustments in subreach location were negligible. We believe therefore that our conclusions were not affected by small biases that may have resulted from shortening the reach in latter years.

### 3.1. Transport simulation

The model One-dimensional Transport with Inflow and Storage with Parameter estimation (OTIS-P) [20] was used to simulate results of all tracer experiments. OTIS-P solves the commonly used governing equations for one-dimensional transport in a stream where exchange occurs with groundwater and “storage” zones. The equations are

\[
\frac{\partial C}{\partial t} = - \frac{Q}{A} \frac{\partial C}{\partial x} + \frac{q_{\text{L}}^\text{in}}{A} (C_L - C) + \frac{q_{\text{L}}^\text{out}}{A} (C_L - C) + \frac{q_{\text{S}}}{A} (C_S - C),
\]

where

- \( C \) is the concentration of the tracer,
- \( Q \) is the streamflow,
- \( A \) is the stream area,
- \( D \) is the stream dispersion,
- \( q_{\text{L}}^\text{in} \) and \( q_{\text{L}}^\text{out} \) are the groundwater inflow and outflow rates, respectively,
- \( C_L \) is the concentration of the tracer in the groundwater,
- \( C_S \) is the concentration of the tracer in the storage zones.

### Table 1
Transport parameters determined from instream tracer injections in Pinal Creek, Arizona

<table>
<thead>
<tr>
<th>Date</th>
<th>Reach length (m)</th>
<th>Upstream streamflow, ( Q ) (m(^3)/s)</th>
<th>Groundwater discharge, ( q_{\text{L}}^\text{in} ) (m(^3)/s)( \times 10^{-5} )</th>
<th>Stream velocity, ( u ) (m/s)</th>
<th>Stream area, ( A ) (m(^2))</th>
<th>Stream dispersion, ( D ) (m(^2)/s)</th>
<th>Storage area, ( A_s ) (m(^2))</th>
<th>Storage exchange, ( a ) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>6/1/94</td>
<td>1140</td>
<td>0.21</td>
<td>1.2( \times 10^{-5} )</td>
<td>0.53</td>
<td>0.35</td>
<td>0.62</td>
<td>0.04</td>
<td>4.2E–04</td>
</tr>
<tr>
<td>6/1/95</td>
<td>234</td>
<td>0.21</td>
<td>7.7( \times 10^{-5} )</td>
<td>0.82</td>
<td>0.27</td>
<td>0.54</td>
<td>0.05</td>
<td>1.7E–03</td>
</tr>
<tr>
<td>5/17/97</td>
<td>323</td>
<td>0.17</td>
<td>9.3( \times 10^{-5} )</td>
<td>0.36</td>
<td>0.43</td>
<td>1.04</td>
<td>0.15</td>
<td>4.7E–04</td>
</tr>
<tr>
<td>6/3/98</td>
<td>153</td>
<td>0.14</td>
<td>9.3( \times 10^{-5} )</td>
<td>0.22</td>
<td>0.62</td>
<td>2.40</td>
<td>0.46</td>
<td>4.5E–04</td>
</tr>
<tr>
<td>6/15/99</td>
<td>83</td>
<td>0.07</td>
<td>2.0( \times 10^{-5} )</td>
<td>0.10</td>
<td>0.63</td>
<td>0.62</td>
<td>0.51</td>
<td>5.6E–04</td>
</tr>
</tbody>
</table>

Fig. 4. Repeat photography showing increasing coverage of aquatic and emergent macrophytes in Pinal Creek, Arizona from June 1995 to June 1999.
\[ \frac{\partial C_i}{\partial t} = x \left( \frac{A}{A_s} \right) (C - C_s), \]  

where \( x \) (m) and \( t \) (s) are distance along a stream and time, respectively; and \( C \), \( C_i \), and \( C_s \) are tracer concentrations in streamwater, storage zones, and groundwater, respectively. \( C \) and \( C_s \) are vertically and horizontally averaged at a stream cross-section for a given distance along the reach, whereas \( C_s \) is a reach-averaged quantity. \( Q \) (m³/s) is streamflow at a cross-section, \( A \) (m²) is the reach-averaged cross-sectional area of the active stream channel, \( D \) (m²/s) is the reach-averaged longitudinal dispersion coefficient, \( q_L^m \) (m³/(m s)) is the reach-averaged groundwater discharge per unit length, \( A_s \) (m²) is the reach-averaged cross-sectional area of the storage zone, and \( x \) (s⁻¹) is the reach-averaged mass transfer coefficient between stream and storage zone. Initial and boundary conditions for the model are discussed by Runkel [20].

A key aspect of the model that helps explain the tracer data is the delay that occurs in downstream transport of tracer due to solute exchange with storage zones. Storage is represented mathematically as first-order exchange of solute between the stream and well-mixed storage zones to the side or beneath the active stream channel. Storage is defined from a modeling perspective as the collection of mixing processes in the channel that cannot adequately be simulated by Fickian dispersion (i.e. through adjustment of the longitudinal dispersion parameter, \( D \)). Model storage zones represent the somewhat slower ‘nonequilibrium’ mixing processes in streams, such as pockets of stagnant or recirculating water in surface water, as well as streamwater that temporarily is routed through subsurface (hyporheic) flow paths before being returned to the channel. Other important characteristics of the storage concept are that solutes are well mixed in storage zones, resulting in an exponential distribution of “storage” times. Also, there is no net transport parallel to the stream of stored solutes. Groundwater discharge and recharge, unlike storage, had little effect on the timing of downstream transport but an important effect on plateau solute concentrations in the stream (discharge), and on solute mass balance (both discharge and recharge).

3.2. Estimating flow and transport parameters

Streamflow and groundwater discharge and recharge were estimated by calculations made directly from tracer data. Steady flow was assumed, and only the tracer samples collected after a constant ‘plateau’ concentration had been achieved were used for the calculations. Fluxes were calculated from the following mass balance equation

\[ Q_{dwn} = Q_{up} + \Delta Q = Q_{up} + q_L^m L - q_L^m L, \]  

where \( Q_{dwn} \) and \( Q_{up} \) are flow at the downstream and upstream endpoints of a study reach of length \( L \), and \( q_L^m \) and \( q_L^m \) are the reach-averaged groundwater discharge and recharge rates, respectively. \( Q_{up} \) is computed by the dilution-gaging method from tracer sampling at the upstream end of the reach, whereas \( Q_{dwn} \) was computed from the decrease in the plateau concentration from upstream to downstream that results from dilution by groundwater. Determining recharge requires an estimate of \( Q_{dwn} \), which was obtained for the downstream end of the reach from the second shorter-term injection. Recharge was computed by rearranging Eq. (3) and solving for \( q_L^m \) as \( \left( (Q_{up} + q_L^m) - Q_{dwn} \right)/L \). Further explanation of the tracer mass balance and calculations are available in [10].

Most of the other transport and storage characteristics of the stream were estimated by “inverse” modeling of the tracer data using OTIS-P. OTIS-P uses a nonlinear least-squares optimization routine (STARPARC) that runs the code numerous times using standard criteria to objectively search for values of parameters that best reproduce field measurements of tracer concentrations. Four of the transport parameters were estimated by inverse modeling; including stream cross-sectional area, \( A \), stream longitudinal dispersion coefficient, \( D \), stream-storage zone exchange coefficient, \( x \), and storage-zone cross-sectional area, \( A_s \). All of the basic modeling results are reported in Table 1.

Channel width, \( w \), and channel slope, \( s \), were the only variables determined from field measurements not involving the tracer data. These variables were estimated by taping and leveling, respectively. Reach-averaged stream depth, \( d \) (m), was computed as \( A/w \). The Darcy–Weisbach friction factor was calculated as,

\[ f = \frac{8gd ds}{u^2}, \]  

where \( g \) is the gravity; \( d \), the stream depth; \( s \), the channel slope; and \( u \), the stream velocity.

3.3. Metrics characterizing solute storage and hydrologic retention

Several computations were made with tracer-modeling parameters to characterize solute storage and hydrologic retention. First was the streamwater turnover length, or the average distance a water molecule travels in the channel before entering the storage zone, \( L_s \) (m) [17]. \( L_s \) is computed as \( u/s \) where \( u \) (m/s) is the reach-averaged stream velocity. Reach-averaged velocity was computed by dividing the average streamflow in the reach, \( Q = (Q_{dwn} - Q_{up})/2 \), by the average stream cross-sectional area, \( A \). Once a water molecule enters the storage zone, it resides there for a period referred to as the storage-zone residence time, \( t_r \) (s) before re-entering the channel [10]. The storage-zone residence time is
computed as the size of the storage zone divided by the flux of streamwater though the storage zone (per unit length of stream), or \( A_s/\dot{Q} \). The other important measure of storage that was important was hydrologic retention, \( R_h \) (s/m) [15], which considers both the average time water spends in storage along with the average distance water travels in the channel before entering the storage zone (i.e. streamwater turnover length). Hydrologic retention is computed from the average storage-zone residence time divided by the streamwater turnover length,

\[
R_h = \frac{A_s}{\dot{Q} L_s}.
\]

(5)

Note that the expression for \( R_h \) can be simplified and computed as \( A_s/\dot{Q} \). Because hydrologic retention characterizes the combined effects of storage and its influence on instream solute transport, it was selected as the primary metric for comparing results from Pinal Creek with other streams.

3.4. Tracer test design and uncertainty estimation

To the extent possible, uncertainties were estimated for all channel and transport parameters. For parameters determined by inverse modeling, uncertainties were obtained directly from the output of the statistical package that accompanies OTIS-P. The uncertainty of average stream widths was estimated as the standard error of approximately 10–15 measured widths in the experimental reach. Uncertainties for variables that were computed by addition or multiplication of other variables (e.g. stream velocity and stream depth) decreased, while the width of the channel and transport parameters. For parameters determined by inverse modeling, uncertainties were obtained directly from the output of the statistical package that accompanies OTIS-P. The uncertainty of average stream widths was estimated as the standard error of approximately 10–15 measured widths in the experimental reach. Uncertainties for variables that were computed by addition or multiplication of other variables (e.g. stream velocity and stream depth) were computed by addition or multiplication of other variables (e.g. stream velocity and stream depth) were computed by addition or multiplication of other variables (e.g. stream velocity and stream depth). Streamflow, stream velocity, and stream depth all decreased, while the width of the stream increased. Average stream velocity decreased by approximately a factor of four, from 0.8 to 0.2 m/s. Stream width increased by approximately a factor of four, from 3 to 13 m. Changes were less for streamflow and stream depth. Streamflow decreased by approximately a factor of three (mainly in the last year of the study period) from 0.2 to 0.07 m²/s. Stream depth also decreased by approximately a factor of two, from 0.09 to 0.04 m.

Storage-zone size and water residence time in storage zones increased substantially between 1994 and 1999 at Pinal Creek. The storage-zone cross-sectional area (\( A_s \)) increased by an order of magnitude, from 0.05 to 0.5 m², at the same time that stream cross-sectional area (\( A \)) only increased by a factor of two, from 0.3 to 0.6 m². As a result, the ratio of storage zone to stream cross-sectional area (\( A_s/A \)) increased significantly from 1994 to 1999, from less than 20% in 1994 to over 80% in 1999. The average residence time of a parcel of water that enters the storage zone (\( t_r \)) increased from 5 min in 1994 to 24 min in 1999. Hydrologic retention, \( R_h \), a measure of the total time a parcel of water spends in storage per meter of downstream transport, increased more than an order of magnitude in the 5-year study period, from 0.2 to 8 s/m.

4. Results

Bromide tracer data and best-fit simulations for three of the five tracer tests (1995, 1997, and 1998) are shown in Fig. 5. Those data are representative of the sampling frequency and goodness of model fit for all years. Fig. 5 also illustrates the general changes that occurred in the shape of the breakthrough curve during the 1990s. The tendency for the breakthrough curves to rise more slowly toward a plateau concentration in later years is an indication of the increasing importance of hydrologic retention of stream water and tracer in storage zones (Fig. 5).

Changes over time in transport and storage parameters are contrasted with changing channel physical characteristics in Fig. 6. Streamflow, stream velocity, and stream depth all decreased, while the width of the stream increased. Average stream velocity decreased by approximately a factor of four, from 0.8 to 0.2 m/s. Stream width increased by approximately a factor of four, from 3 to 13 m. Changes were less for streamflow and stream depth. Streamflow decreased by approximately a factor of three (mainly in the last year of the study period) from 0.2 to 0.07 m²/s. Stream depth also decreased by approximately a factor of two, from 0.09 to 0.04 m.

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5. Predicting changes in hydrologic retention

At Pinal Creek both hydrologic retention and the Darcy–Weisbuch friction factor increased by an order of magnitude or more between 1994 and 1999, while streamflow decreased only by approximately a factor of two. When compared with other channels where repeat
tracer experiments were conducted, Pinal Creek showed the greatest change in hydrologic retention for a given change in streamflow (Fig. 7). Tracer test results from four other streams were acquired from the published literature, including data from Gallina Creek, NM [15], Lookout Creek, OR [3], Walker Branch, TN [18], and St. Kevin Gulch, CO [9]. The four other streams are generally located in forested mountain areas with a relatively high stream gradient, which contrasts with the semi-arid alluvial setting at Pinal Creek. Pools and riffles are present in all streams, but these features are much less common in Pinal Creek. Another important difference is that while the four other streams mainly experienced changes in streamflow between tracer studies, Pinal Creek experienced a dramatic expansion of aquatic vegetation and channel widening and shallowing.

Based on linear regression using log-transformed variables, streamflow, $Q$, and friction, $f$, are both rea-
Friction are negatively correlated \( (r) \) predictor of hydrologic retention \( (\text{all tracer studies). Friction is marginally a better pre-

Creek, NM \[15\], and St. Kevin Gulch, CO \[9\].

follows: Walker Branch, TN \[18\], Lookout Creek, OR \[3\], Gallina Creek, NM \[15\], and St. Kevin Gulch, CO \[9\].

A statistical test indicated that the slope of the regression for all other data. Sources of data from other streams are as follows: Walker Branch, TN \[18\], Lookout Creek Reach 4, OR \[4\], Lookout Creek Reach 7, OR \[6\], and Walker Branch, TN \[8\].

Fig. 7. Changes in hydrologic retention compared with changes in streamflow for five streams in the United States. Data were normalized by dividing by geometric mean values for each stream. One regression line is shown for Pinal Creek data while another regression line is shown for all other data. A statistical test indicated that the slope of the regression for Pinal Creek differs significantly from the slope of the regression for all other data. Sources of data from other streams are as follows: Walker Branch, TN \[18\], Lookout Creek, OR \[3\], Gallina Creek, NM \[15\], and St. Kevin Gulch, CO \[9\].

reasonably good predictors of hydrologic retention across all tracer studies. Friction is marginally a better predictor of hydrologic retention \( (R^2 = 0.57, \text{SE} = 0.61, F\text{-statistic} = 20.05, p < 0.0004, \text{df} = 16) \) compared with streamflow \( (R^2 = 0.55, \text{SE} = 0.63, F\text{-statistic} = 18.2, p < 0.0007, \text{df} = 16) \). Not surprisingly, streamflow and friction are negatively correlated \( (r = -0.7) \), because the Darcy–Wiesbach friction factor also contains information about stream size. In addition to differing in the sign of their relationship with hydrologic retention, streamflow and friction have some independent statistical capability in predicting hydrologic retention. This is shown by a two-predictor model for hydrologic retention that had higher \( R^2 \) (0.66), lower SE (0.57), and a significant effect of each variable at the 0.1 level or better \( (p < 0.05 \text{ for } f \text{ and } 0.08 \text{ for } Q) \).

\[
\log(R_b) = 0.3089 \log(f) - 0.3742 \log(Q) - 0.45. \tag{6}
\]

5.1. Independent effects of streamflow and friction on hydrologic retention

We interpret the independent effects of streamflow and friction as predictors of hydrologic retention as follows: (1) higher streamflow increases the amount of streamwater that must be exchanged with storage zones in order to affect downstream transport of solute, while (2) higher friction reflects greater storage-zone size and longer residence time. Stream size is important because streamflow often increases by orders of magnitude during a storm, which vastly increases the amount of water that will be potentially be delayed by interaction with storage zones. The storage zones themselves are typically not as responsive to storms and often decline rather than increase in size during or following a storm \([9,29,32]\). Nevertheless, this degree of change in storage-zone size does matter in the effect that it has on downstream transport. Friction is a good candidate for an indicator of storage processes, because it is a force that plays a direct role in creating some of the zones that store solute, i.e., stagnant or recirculating flow zones adjacent to and behind roughness features. Solute is also stored in subsurface (hyporheic) flow paths, which also relates to frictional resistance because higher friction is associated with greater unevenness in the pressure distribution at the sediment boundary that drives surface–subsurface hydraulic exchange \([19]\). In summary, while streamflow and friction are themselves correlated, each has some independent statistical power as a predictor of hydrologic retention. Independence between streamflow and friction in their combined relationship with hydrologic retention partly reflects the closer association of the friction estimate with properties of the storage zones themselves.

The best means to visualize the independent effects of streamflow and friction requires that values of \( Q, f, \) and \( R_b \) computed from repeat tracer experiments be normalized by dividing by geometric mean values for that stream. Note that there appears to be considerable variability in the slope of the relation between hydrologic retention and streamflow for different streams (Fig. 7). In particular, the relationship between hydrologic retention and streamflow is steeper for Pinal Creek compared with other streams, which means that hydrologic retention at Pinal Creek changed much more for a given change in streamflow compared with other streams. This difference is further illustrated by the statistically significant difference in the slope of the relationship between hydrologic retention and streamflow for Pinal Creek compared with the relationship for the rest of the streams \( (t\text{-statistic} = 4.6, p < 0.01, \text{df} = 4) \).

Variability was not nearly as great between slopes of the hydrologic retention and friction relationships at Pinal Creek compared with other streams. This is illustrated by a slope for the hydrologic retention and friction relationship at Pinal Creek that was statistically indistinguishable \( (t\text{-statistic} = 0.53, p < 0.3, \text{df} = 4) \) from the slope of a relationship developed for the other four streams (Fig. 8). Finding that the slopes of retention–friction relationships for individual streams are indistinguishable contrasts sharply with results using streamflow as the predictor variable. We conclude that friction is a more reliable predictor of changes in hydrologic retention, especially in streams that have undergone significant adjustments in channel features.

Relationships between hydrologic retention and friction have their greatest statistical significance when variables are normalized. The drawback of using the
A measure of reach-averaged frictional resistance is a good predictor of hydrologic retention. Friction is a force that is closely interrelated with several stream variables, including stream gradient, stream velocity, flow depth, and drag forces across individual roughness features. When averaged over a stream reach, friction is often closely related to the height to which roughness features such as cobbles and sandbars protrude into the flow [1]. In addition to affecting the mean depth and mean velocity of streams, friction also promotes solute exchange by incorporating more predictor variables.

6. Discussion

Why were increases in hydrologic retention so large at Pinal Creek compared to the other four streams? The four other streams mainly experienced changes in streamflow while Pinal Creek experienced expanding coverage of aquatic vegetation that caused channel widening. The key factor driving the expansion of aquatic vegetation appears to have been a temporary decrease in sediment storage in streams, by creating zones of flow separation and solute exchange. Stream water flowing across roughness elements on the streambed such as boulders and sandbars creates an uneven pressure distribution at the sediment boundary that drives hydraulic exchange between stream water and porewater, resulting in temporary storage of solutes in the hyporheic zone [19].

Why were increases in hydrologic retention so large at Pinal Creek compared to the other four streams? The four other streams mainly experienced changes in streamflow while Pinal Creek experienced expanding coverage of aquatic vegetation that caused channel widening. The key factor driving the expansion of aquatic vegetation appears to have been a temporary decrease in the occurrence of floods during the 1990s. Several years without floods allowed aquatic macrophytes to continue expanding without the usual flood-induced removal during summer monsoons. The physical response of the channel to increasing drag forces on plant stems was widening and shallowing rather than deepening. The banks in Pinal Creek are low in height and unconsolidated either by fine grains or extensive riparian roots systems, and therefore the banks are easily eroded when water is forced against them by the increasing biomass of aquatic vegetation. Sediment supply in this alluvial system also is not lacking, with an abundant upstream supply of coarse sediment from the alluvial system, as well as a new source of organic sediment from decaying plants. New sediment raises the bed elevation of the stream and promotes channel widening by allowing the banks to be overtopped. Our observations are consistent with those of Huang and Nanson [11] who noted the effect of aquatic vegetation in promoting channel widening in some dryland rivers of Australia. In contrast, in humid areas of the world the effect of expanding aquatic vegetation in channels more typically has been the opposite effect of what we observed at Pinal Creek, i.e.
changes at once, including changes in streamflow, develop a model that could predict all the relevant desirable goal, which is not yet obtainable, would be to dated friction and streamflow measurements). A more only after channel changes have occurred (using up-

dependable predictions of storage conditions, at least for one component of stor-

generated databases. Achieving that level of rigor and generality is a formidable challenge. Consider, for example, how difficult it would be to develop a simula-
tion model that incorporates all of the hydrologic, geomorphic, and biological factors that affect hydro-
logic retention at Pinal Creek. Even considering a subset of that problem is a significant challenge. Most progress to date involves improving physically based modeling of friction for very specific circumstances (e.g. boulder-bed, sand-bed, vegetation-choked, etc.), and those theories still tend to involve one or more empirical parameters that must be calibrated for specific circumstances [1]. Physically based modeling of solute storage is no less difficult of a problem, although progress is being made on specific aspects of the problem such as modeling hyporheic flow through streambeds [8,19,29]. More recently, Worman et al. [31] developed scaling relation-
ships for storage characteristics of natural streams that relate the empirical parameters determined from stream tracer experiments to more physically-based parameters of the advective pumping model of hyporheic exchange developed in laboratory flumes. Although still largely empirical, the latter approach has promise for building more of a physical basis into predictions of changing storage conditions, at least for one component of storage, i.e. exchange between stream and streambed hyporheic zone.

7. Conclusions, implications, and future needs

Streamflow is a useful predictor of hydrologic retention in streams because it determines how much water the storage zones must process in order for downstream transport to be measurably delayed. For example, larger streams need larger storage zones (with an equal amount of flow through them) in order to impart the same delay to downstream solute transport as a smaller stream. Our work showed that the Darcy–Weisbach friction factor adds important independent information about the storage zones themselves to predictive equations. Fric-
tion is the best single predictor, while a two-predictor regression model, with friction and streamflow each contributing some independent explanatory capability, provides the most accurate prediction of hydrologic retention. The two-predictor regression relationship in Eq. (6) is particularly useful, because friction and streamflow are easily estimated from field measurements whereas hydrologic retention is not. Because our approach was tested for a diverse set of streams, including pool-riffle streams with boulder beds, streams with sand and fine gravel beds, and streams choked with dense stands of macrophytes, the predictive relationship appears to be relatively robust in characterizing order of magnitude changes in hydrologic retention across a wide variety of channel types.

Despite progress there remain substantial limitations to our predictive approach. The principal limitation is that the prediction is post-hoc, because changes in hydrologic retention are predictable with this method only after channel changes have occurred (using up-
dated friction and streamflow measurements). A more desirable goal, which is not yet obtainable, would be to develop a model that could predict all the relevant changes at once, including changes in streamflow, channel geomorphology and vegetation, and hydrologic retention. Only a small step was made toward that goal, but our interpretation of the relationship between hydrologic retention and reach-averaged friction will help guide future efforts to develop more physically based models of solute storage in streams. The practical outcome of the work is a predictive equation that allows hydrologic retention to be estimated in many different types of channels from relatively simple estimates of friction and streamflow.

An obvious need for future work is more physically based modeling of hydrologic retention in streams. Models for frictional resistance that are both physically based and broadly applicable across many channel types are generally not available. Achieving that level of rigor and generality is a formidable challenge. Consider, for example, how difficult it would be to develop a simula-
tion model that incorporates all of the hydrologic, geomorphic, and biological factors that affect hydro-
logic retention at Pinal Creek. Even considering a subset of that problem is a significant challenge. Most progress to date involves improving physically based modeling of friction for very specific circumstances (e.g. boulder-bed, sand-bed, vegetation-choked, etc.), and those theories still tend to involve one or more empirical parameters that must be calibrated for specific circumstances [1].

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