The role of topography on catchment-scale water residence time

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[1] The age, or residence time, of water is a fundamental descriptor of catchment hydrology, revealing information about the storage, flow pathways, and source of water in a single integrated measure. While there has been tremendous recent interest in residence time estimation to characterize watersheds, there are relatively few studies that have quantified residence time at the watershed scale, and fewer still that have extended those results beyond single catchments to larger landscape scales. We examined topographic controls on residence time for seven catchments (0.085–62.4 km²) that represent diverse geologic and geomorphic conditions in the western Cascade Mountains of Oregon. Our primary objective was to determine the dominant physical controls on catchment-scale water residence time and specifically test the hypothesis that residence time is related to the size of the basin. Residence times were estimated by simple convolution models that described the transfer of precipitation isotopic composition to the stream network. We found that base flow mean residence times for exponential distributions ranged from 0.8 to 3.3 years. Mean residence time showed no correlation to basin area (r² < 0.01) but instead was correlated (r² = 0.91) to catchment terrain indices representing the flow path distance and flow path gradient to the stream network. These results illustrate that landscape organization (i.e., topography) rather than basin area controls catchment-scale transport. Results from this study may provide a framework for describing scale-invariant transport across climatic and geologic conditions, whereby the internal form and structure of the basin defines the first-order control on base flow residence time.


1. Introduction

[2] The process conception of water flow paths and storages in catchment hydrology has been largely influenced by detailed field investigations at disparate site locations. This has limited our capability to develop scaling relationships that are consistent with the complex hydrological processes observed at these sites and elsewhere in nature. The organization of field observations into a hierarchy of importance at different scales has proven difficult [Bonell, 1998; Siddle et al., 2000; Sivapalan, 2003] and characterizing even simple, extremely well instrumented hillslopes and small catchments has been a challenge for hydrologists [Anderson et al., 1997; Hooper, 2001; McGlynn et al., 2002]. This fact has hindered the ability to explain and predict how patterns and processes change across scale. Ultimately, advances in measurement technologies and field observations lag behind the current theoretical framework to scale hydrological processes, which questions how process-level observation can be used in mesoscale (e.g., 100 to 1000 km²) modeling efforts and management programs. Many properties for which scaling relationships have been developed do not lend themselves to verification, since properties such as hydraulic conductivity measured at small scales (e.g., 0.1 to 10s m²) become effective properties determined through model calibration at larger scales.

[3] Tracers have provided some of the most important insights into hydrological processes; from the definition of groundwater and surface water age, to hydrograph source components, to descriptions of water flow pathways at the larger integrative catchment scale [Dincer and Davis, 1984; Buttle, 1994; Kendall and McDonnell, 1998; McDonnell et al., 1999; Uhlenbrook et al., 2002; Soulsby et al., 2004]. Therefore tracer techniques provide an opportunity to examine how flow systems scale based on field observations that describe mechanisms operating within catchments. Tracers allow us to estimate the age or residence time of water in the catchment, revealing information about the storage, flow pathways and source of water in a single measure. Stable isotopes of water (18O and 2H) have been used for the estimation of residence times of <5 years, while...
tritium ($^3$H) is often used to estimate residence times $>5$ years [DeWalle et al., 1997; Maloszewski et al., 1983; Uhlenbrook et al., 2002].

The residence time (or distribution of residence times) of water draining a catchment not only has important implications for flow pathways and storage, but for its water quality, since many biogeochemical reactions are time-dependent [e.g., Hornberger et al., 2001; Burns et al., 2003]. The contact time with subsurface materials has direct control on chemical composition and biogeochemical processes. Additionally, the residence time indicates the catchment’s memory to past inputs and can thus be used as a proxy to understand the hydrologic sensitivity to land use and climate change and other impacts such as its vulnerability to contamination. Understanding how residence time scales is crucial for a variety of biogeochemical and hydrological applications.

Knowledge of how residence time scales would also help illuminate processes that control subsurface flow routing since the residence time is directly related to the diversity of flow pathways in a catchment [Pearce et al., 1986; McDonnell et al., 1991; Kirchner et al., 2001]. Describing processes for large-scale catchments is necessary for developing more understanding-based models that can be used to address questions of practical importance at scales that affect land management and climate change issues. The challenge is how we define model structures for mesoscale prediction where observations may be limited [Sivapalan, 2003]. Residence times can be used to constrain parameterizations for storage in conceptual rainfall-runoff models and provide a process basis for the structure of the model [Uhlenbrook et al., 2000]. The incorporation of residence time estimates and their uncertainty may lead to better predictions of water and solute flux from hydrological models.

While there has been tremendous recent interest in residence time estimation to characterize catchments [e.g., Gibson et al., 2002; Hooper, 2004], there are relatively few studies that have quantified residence time at the catchment scale, and fewer still that have extended those results beyond single catchments to larger landscape scales. We argue that the relationships between stream water residence time and landscape characteristics provide an opportunity to transfer information from one spatial scale to another. However, the scaling of residence time has been only recently addressed in a few studies [McGlynn et al., 2003; Rodgers et al., 2005]. McGlynn et al. [2003] did not find a relationship with catchment scale and residence time, but with the nature of area accumulation within catchments. Only four catchments were evaluated in their study; however, results from Rodgers et al. [2005] provide further support that residence time does not scale with catchment size. Several studies have also examined the residence time of water in hillslopes and found a dependence on accumulated area [Stewart and McDonnell, 1991; Rodhe et al., 1996] and contribution of bedrock seepage [Asano et al., 2002]. These studies suggest that the controls on catchment-scale residence time are complex.

In this paper, residence time is estimated for a set of seven nested catchments using simple flow models that interpret stable isotope variations of rainfall and runoff. We use the results from residence time models to address the following questions: (1) Is stream water residence time related to the size of the catchment? (2) Does topography exert a control on the residence time? (3) Is there a relationship that links residence time across scale? Our primary objective was to determine the dominant control on catchment-scale residence time and provide a simple framework to regionalize those results within a mesoscale basin (62 km$^2$).

2. Site Description

The study catchments are located within the H.J. Andrews Experimental Forest (HJA) in the central western Cascades of Oregon, USA (44.2°N, 122.2°W) (Figure 1). The main drainage within the HJA is Lookout Creek (LOOK, 62.42 km$^2$), which is a tributary to Blue River and eventually the McKenzie River within the Willamette River Basin. Past hydrologic investigations at HJA have focused on the effects of forest management activities on water yield [Rothacher, 1965], peak flows [Harr and McCorison, 1979; Jones and Grant, 1996], snowmelt and accumulation [Harr, 1986; Berris and Harr, 1987], and catchment nutrient budgets [Sollins et al., 1980]. Detailed site descriptions of the overall HJA and the small basins are given by Rothacher et al. [1967], Jones and Grant [1996], and Jones [2000].

Catchments areas (see Figure 1) range from 0.085 to 62.42 km$^2$ and span the climatic, geomorphic, and topographic settings found within the overall LOOK basin (see Table 1). This study focuses on seven catchments within the HJA (WS02, WS03, WS08, WS09, WS10, MACK, and LOOK). While WS09 and WS10 lie immediately outside of LOOK, they represent catchments of similar drainage area and geomorphology to those contained in the lower portion of LOOK.

Lower elevation areas are dominated by Douglas fir (Pseudotsuga menziesii), western hemlock (Tsuga heterophylla), and western redcedar (Thuja plicata) and upper elevation forests contain noble fir (Abies procera), Pacific silver fir (Abies amabilis), Douglas fir, and western hemlock. The coniferous forest landscape is underlain at its lower elevation (<760 m) by mainly Oligocene-lower Miocene formations of volcanic origin, consisting of massive

Figure 1. Map of the H.J. Andrews Experimental Forest showing the locations of the study catchments.
tuffs and breccias derived from mudflows and pyroclastic flows [Swanson and James, 1975]. In higher-elevation areas (>1200 m), bedrock is composed of andesitic/basaltic lava flows of Pliocene age [Sherrod and Smith, 2000]. The intermediate elevations transition from welded and non-welded ash flows to basalt and andesite lava flows. Additionally, glacial, alluvial, and mass movement processes have created deeply dissected, locally steep drainage systems and variable regolith depth [Swanson and James, 1975]. Hillslopes of the lower-elevation catchments (e.g., WS02, WS03, WS09, and WS10) are short (<200 m) and steep (22 to 48°), with local relief of between 60–130 m. Upper elevation catchments (e.g., WS08) are characterized by more gentle (11 to 22°), longer hillslopes (>250 m).

Soils are mainly poorly developed Inceptisols with local areas of Alfisols and Spodosols containing thick organic horizons that have developed over highly weathered parent materials [Dyrness, 1969; Legard and Meyer, 1973; Ranken, 1974]. Although the <2 mm soil fractions are generally composed of a clay loam texture, the soils exhibit massive well aggregated structure that affect hydrologic properties: high infiltration rates (typically >500 cm/h), high drainable porosity (between 15% and 30%), and sharply declining water retention curves [Dyrness, 1969; Ranken, 1974; Harr, 1977]. Overland flow has not been observed on soils in any of the watersheds.

Average annual precipitation varies with elevation from about 2300 mm at the base to over 3550 mm at upper elevations, falling mainly between November and April (~80% of annual precipitation) during frequent long-duration, low-to-moderate-intensity frontal storms. The Mediterranean climate has wet, mild winters and exceptionally dry, cool summers. Low-elevation (430 m) mean monthly temperature ranges from near 1°C in January to 18°C in July. Rainfall predominates at low elevations and snow is more common at higher elevations (e.g., WS08 and MACK). On average, 56% (28 to 76%) of the annual precipitation becomes runoff, which is highly responsive and dominated by average quickflow ratios (38%) that are among the highest reported in the literature [e.g., Hewlett and Hibbert, 1967; McGlynn et al., 2002].

3. Methodology

3.1. Field Measurements

Precipitation samples were collected weekly from January 2000 to February 2003 (~1130 day period) in bulk collectors at two locations that coincided with a low (PRIMET, 430 m) and high (Hi-15, 922 m) elevation meteorological station. Precipitation samplers consisted of plastic funnels with drainage tubing attached to plastic bottles. To minimize evaporation, water traps were created by looping drainage tubes and protecting collection bottles in either a climate controlled shelter (Hi-15) or by burying the bottle beneath the soil surface below a small insulated shelter (PRIMET). Precipitation rates were determined using heated tipping bucket rain gauges at each station as part of HJA long-term data collection. Snowmelt sampling occurred weekly at Hi-15 during the 2001–2002 winter using a 0.25 m² snow lysimeter that drained into a heated shelter to prevent the samples from freezing. Snowmelt rates were measured using tipping buckets (0.025 mm per tip) and a 5.52 m² lysimeter. A network of small bulk rainfall collectors (N = 38) were used to assess input variations across the large basin scale for 3 rain storms in fall 2002. Seven stream sites (WS02, WS03, WS08, WS09, WS10, MACK, and LOOK) were sampled weekly (generally on the same day as precipitation sample collection). Since weekly precipitation samples represent volume-weighted averages over the preceding week, samples that were collected within a 24-hr window of an event were not used in the analysis. Therefore the following analysis pertains only to timescales longer than one week.

Samples collected prior to October 2000 were analyzed at the Colorado State University facility for Mass Spectrometry and after October 2000, at the USGS Stable Isotope Laboratory in Menlo Park, California for oxygen-18 composition (δ¹⁸O) using an automated version of the CO₂–H₂O equilibration technique of Epstein and Mayeda [1953]. The δ¹⁸O values are reported in per mil (%) relative to a standard as δ¹⁸O = (R₀/R − 1) × 1000, where R₀ and R are the ¹⁸O/¹⁶O ratios for the sample and standard (VSMOW), respectively. The analytical precision (σ) was 0.11% based on submitted blind duplicate samples.

3.2. Input Characterization

The input δ¹⁸O for each catchment was adjusted for an elevation effect [cf. Dansgaard, 1964] based on the two (high/low elevation) sampling stations. For catchments with significant seasonal snowpack (WS08, MACK, and LOOK), the Hi-15 station was used as the reference input signal, which included snowmelt rates and isotopic composition when a snowpack was present, while low-elevation catchments (WS02, WS03, WS09, and WS10) used the PRIMET station as the reference input signal. The input

### Table 1. Geologic and Geomorphic Catchment Descriptions

<table>
<thead>
<tr>
<th>Catchment</th>
<th>Area, km²</th>
<th>Mean Slope, deg</th>
<th>Minimum Elevation, m</th>
<th>Maximum Elevation, m</th>
<th>Geologic/Geomorphic Description*</th>
</tr>
</thead>
<tbody>
<tr>
<td>WS02</td>
<td>0.601</td>
<td>27</td>
<td>548</td>
<td>1070</td>
<td>97% steep volcaniclastics, 3% fractured andesitic/basaltic lava flows and soils &lt;1 m</td>
</tr>
<tr>
<td>WS03</td>
<td>1.011</td>
<td>26</td>
<td>418</td>
<td>1080</td>
<td>68% steep volcaniclastics with &lt;1 m soils, 22% earthflow with &gt;3 m soils, 10% fractured andesitic/basaltic lava flows</td>
</tr>
<tr>
<td>WS08</td>
<td>0.214</td>
<td>15</td>
<td>993</td>
<td>1170</td>
<td>55% Benchy volcaniclastics and glaciated till/colluvium, 45% earthflow with &gt;3 m soils, 24% glaciated till/colluvium</td>
</tr>
<tr>
<td>WS09</td>
<td>0.085</td>
<td>31</td>
<td>432</td>
<td>700</td>
<td>99% steep volcaniclastics with &lt;1 m soils</td>
</tr>
<tr>
<td>WS10</td>
<td>0.102</td>
<td>29</td>
<td>473</td>
<td>680</td>
<td>92% steep volcaniclastics, with basaltic/ryolitic dikes and 1–3 m soils</td>
</tr>
<tr>
<td>MACK</td>
<td>5.81</td>
<td>25</td>
<td>758</td>
<td>1610</td>
<td>82% steep volcaniclastics with &lt;1 m soils, 18% fractured andesitic/basaltic lava flows</td>
</tr>
<tr>
<td>LOOK</td>
<td>62.42</td>
<td>20</td>
<td>428</td>
<td>1620</td>
<td>all of the above including large alluvial stream terraces, ~1–3 m soils</td>
</tr>
</tbody>
</table>

*Information compiled from a variety of resources including Swanson and James [1975], Legard and Meyer [1973], Dyrness [1969], and Harr [1977].


\[ \delta_{in}(t) = \left( E_R - E_{ref} \right) S(t) + \delta^{18}O_{ref}(t) \]  

where \( \delta_{in} \) is the catchment specific \( \delta^{18}O \) input, \( E_R \) is the effective catchment recharge elevation and a fitting parameter, \( E_{ref} \) is the elevation of the reference precipitation station, \( S \) is the isotopic difference between Hi-15 and PRIMET stations normalized by their elevation for each of the sampling periods. This was computed as a simple linear interpolation:

\[ \delta_{wo}(t) = (E_R - E_{ref})S(t) + \delta^{18}O_{ref}(t) \]  

where \( \delta_{in} \) is the catchment specific \( \delta^{18}O \) input, \( E_R \) is the effective catchment recharge elevation and a fitting parameter, \( E_{ref} \) is the elevation of the reference precipitation station, \( S \) is the isotopic difference between Hi-15 and PRIMET stations normalized by their elevation difference, and \( \delta^{18}O_{ref} \) is the measured isotopic composition for the reference station. The isotopic difference term \( S \) is time-dependent (i.e., varies with sample collection period), since the elevation effect can vary in time. When a catchment effective recharge elevation equals the elevation of the reference precipitation station, then the measured isotopic composition for that station is used as input for that catchment. An elevation effect is only invoked when a calibrated effective recharge elevation is greater than the elevation of the reference precipitation station.

[16] Residence time studies often suffer from short input records, which yield nonunique model calibrations or uncertain parameter estimates of the residence time distribution. Many investigators have extended stable isotope inputs using regression models with temperature records [Burns and McDonnell, 1998; Uhlenbrook et al., 2002], annual sinusoidal components [McGuire et al., 2002], or data from nearby long-term stations [Maloszewski et al., 1992; Vitvar and Balderer, 1997]. In our study, complex topography and the lack of strong seasonal \( \delta^{18}O \) fluctuations in precipitation precluded the two latter approaches. We examined several regression models based on temperature, precipitation, wind direction (a surrogate for storm track), and interactions of these variables, but at best could not explain more than 30% of the observed \( \delta^{18}O \) variation. Inputs prior to January 2000 were roughly approximated by assuming that the mean base flow (i.e., groundwater) \( \delta^{18}O \) of each catchment reflects the long-term average input \( \delta^{18}O \). In general, the seasonality of precipitation limits recharge to the winter; thus causing an effectively constant \( \delta^{18}O \) input. A warm-up period of ten months was used to minimize potential effects of the assumed constant input on the residence time calibration (see the range of measured streamflow \( \delta^{18}O \) in Figure 2). The past inputs allowed us to examine residence times that were greater than the length of time for which precipitation \( \delta^{18}O \) was measured (~1130 days). It can be shown for all sites where there is no elevation effect on the precipitation \( \delta^{18}O \), that the long-term weighted \( \delta^{18}O \) of precipitation is approximately equal to the mean base flow composition. Precipitation sampled at PRIMET in this study and by Welker [2000] had a weighted mean \( \delta^{18}O \) of ~-10.46‰. The base flow mean \( \delta^{18}O \) for corresponding sites (i.e., similar elevation) was ~-10.61 and ~-10.84‰ for WS09 and WS10, respectively. At the high-elevation site (Hi-15), the weighted mean \( \delta^{18}O \) was ~-11.43‰ which was comparable to the mean base flow \( \delta^{18}O \) in WS08 of ~-11.27‰.

### 3.3. Residence Time Modeling Theory and Approach

[17] The tracer composition of precipitation that falls on a catchment will be delayed by some timescale(s) before reaching the stream. More explicitly, the stream outflow composition at any time, \( \delta_{out}(t) \), consists of past inputs lagged, \( \delta_{out}(t - \tau) \), according to their residence time distribution, \( g(\tau) \) [Dincer et al., 1970; Maloszewski and Zuber, 1982; Richter et al., 1993]:

\[ \delta_{out}(t) = \int_0^{\infty} g(\tau)\delta_{wo}(t - \tau)d\tau \]  

where \( \tau \) are the lag times between input and output tracer composition. This model is similar to the linear system approach used in unit hydrograph models [e.g., Dooge, 1973]; however, only tracer is considered here and thus \( g(\tau) \) represents the tracer transfer function (see discussion below). Equation (2) is valid only for systems at steady state or when the mean flow pattern does not change significantly in time [Zuber, 1986]. It can be reexpressed with both \( t \) and \( \tau \) corrected as flow time [Rodhe et al., 1996]:

\[ t_c = \int_0^{t} Q(t)dt/\bar{Q} \]  

where \( t_c \) is flow-corrected time and \( \bar{Q} \) is the mean annual flow. Accordingly, the assumption of time invariance holds, since \( t_c \) is proportional to the flow rate relative to the mean annual flow. We used both expressions of time in equation (2) and obtained similar fits to our stream isotope data. Kirchner et al. [2000, 2001] also found that a similar time transformation yielded equivalent results to equation (2). Therefore, in this study we used the strict time-based approach since interpretation is more straightforward. This assumes an average residence time distribution for the study period, even though the precipitation seasonality suggests a time variant distribution. However, because the temporal precipitation
pattern is the same for all catchments, the results are relatively comparable. [18] The convolution equation (2) must also include recharge weighting \( w(t - \tau) \) so that the streamflow composition reflects the mass flux leaving the catchment [Stewart and McDonnell, 1991; Weiler et al., 2003]:

\[
\delta_{\text{out}}(t) = \frac{\int_0^\infty g(\tau)w(t-\tau)\delta_{\text{in}}(t-\tau)d\tau}{\int_0^\infty g(\tau)w(t-\tau)d\tau}
\]  

(4)

This modification is more flexible than other recharge adjustment techniques [Grabczak et al., 1984; Maloszewski et al., 1992] and allows for any appropriate factor to be used such as rainfall rates, throughfall rates, or partially weighted rainfall rates (e.g., effective rainfall). In our case, measured daily precipitation/snowmelt rates were used for \( w(t) \) since the seasonality of precipitation/snowmelt and recharge are strongly correlated at HJA. Nonetheless, we examined more complex models to estimate effective precipitation using simple rainfall-runoff transfer functions (i.e., unit hydrograph approaches [see Weiler et al., 2003]), but these did not yield different residence times and the increased number of parameters increased the overall model uncertainty. Different realizations of the recharge term had little effect on the estimates of residence time. This is likely an effect of the Mediterranean climate, where the high evapotranspiration demand coincides with a period of little rainfall. From equation (4) (and (2)) it is clear that \( g(\tau) \) must sum to unity to conserve mass. [19] The travel time or residence time distribution (RTD) or \( g(\tau) \) describes the fractional weighting of how mass (i.e., tracer) exits the system, which is equivalent to the probability density function (pdf) or transfer function of tracer applied to the catchment. If the tracer is conservative and there are no immobile zones in the catchment, then the tracer RTD is equal to the water RTD or the mean residence time of tracer is equal to the mean residence time of water \( (V_m/Q, \text{where } V_m \text{ is the volume of mobile water and } Q \text{ is the volumetric flow rate through the system}) \). Our definition of residence time herein is the time elapsed since the water molecule entered the catchment as recharge to when it exits at some discharge point (i.e., catchment outlet, monitoring well, soil water sampler, etc.) [Bethke and Johnson, 2002; Etchevery and Perrochet, 1999; Rodhe et al., 1996]. RTDs used in equations (2) and (4) are time-invariant, spatially lumped characteristics of the catchment. [20] It is important to note that the timescale of the runoff response is different than the residence time because fluctuations in hydraulic head (the driving force in water flux) can propagate much faster than the transport of conservative tracer or individual water molecules [see Weiler et al., 2003]. Thus the timescales between the rainfall-runoff response and transport (i.e., residence time) are effectively decoupled [Williams et al., 2002]. This partially explains why the majority of a storm flow hydrograph is composed of “old” water [Buttle, 1994; Richey et al., 1998; Kendall and McDonnell, 1998] even though runoff response to rainfall is often immediate [Kirchner, 2003]. [21] A catchment’s RTD could have various shapes depending on the exact nature of its flow path distribution and flow system. Distributions that were evaluated in this study are shown in Table 2. They include the exponential and exponential-piston flow distributions, which represent the apparent behavior of a well-mixed linear reservoir or a delayed linear reservoir, respectively [Maloszewski and Zuber, 1982; Rodhe et al., 1996]. The exponential distribution is the most widely used distribution in catchment systems [Hajtjema, 1995; DeWalle et al., 1997; Amin and Campana, 1996; Burns et al., 1998; Buttle et al., 2001]. Other distributions such as the dispersion and gamma have been used successfully in several catchment studies as well [Maloszewski and Zuber, 1982; Maloszewski et al., 1983; Vitvar and Balderer, 1997; Kirchner et al., 2000]. The dispersion distribution is the one-dimensional solution to

<table>
<thead>
<tr>
<th>Model</th>
<th>Residence Time Distribution</th>
<th>Parameters</th>
<th>Mean Residence Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exponential&lt;sup&gt;b&lt;/sup&gt;</td>
<td>( \tau_m^{-1} \exp(-\tau/\tau_m) )</td>
<td>( \tau_m )</td>
<td>( \tau_m )</td>
</tr>
<tr>
<td>Exponential-piston flow&lt;sup&gt;b&lt;/sup&gt;</td>
<td>( \left( \frac{\tau}{\tau_m} \right)^{-1} \exp\left( -\frac{\tau}{\tau_m} + \eta - 1 \right) ) for ( \tau \geq \tau_m (1 - \eta^{-1}) )</td>
<td>( \tau_m, \eta )</td>
<td>( \tau_m )</td>
</tr>
<tr>
<td></td>
<td>( 0 ) for ( \tau &lt; \tau_m (1 - \eta^{-1}) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dispersion&lt;sup&gt;b&lt;/sup&gt;</td>
<td>( \left( \frac{4\alpha\beta}{\tau_m^2} \right)^{-1/2} \tau^{-1} \exp\left( -\left( 1 - \frac{\tau}{\tau_m} \right)^2 \frac{4\alpha}{4\beta+\tau_m^2} \right) )</td>
<td>( \tau_m, D_p )</td>
<td>( \tau_m )</td>
</tr>
<tr>
<td>Gamma&lt;sup&gt;a&lt;/sup&gt;</td>
<td>( \omega \exp\left( -\frac{t}{\tau_p} \right) + \frac{\tau_p}{\tau_p} \exp\left( -\frac{t}{\tau_p} \right) )</td>
<td>( \tau_p, \tau_r, \phi )</td>
<td>-</td>
</tr>
<tr>
<td>Two parallel linear reservoirs&lt;sup&gt;e&lt;/sup&gt;</td>
<td>( \frac{s^a}{(s+1)^a} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Power law&lt;sup&gt;f&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>No characteristic residence time is associated with the power law model; the two parallel linear reservoirs model was calculated numerically by the first moment.

<sup>b</sup>Maloszewski and Zuber [1982].

<sup>c</sup>Kirchner et al. [2001].

<sup>d</sup>Weiler et al. [2003].

<sup>e</sup>Schumer et al. [2003].
the advection-dispersion equation assuming that tracer is introduced and sampled in proportion to volumetric flow [Kreft and Zuber, 1978]. The gamma distribution, which has been used widely in unit hydrograph modeling [cf. Dooge, 1973], was demonstrated by Kirchner et al. [2000] to consistently represent the RTD for several catchments in Wales. Using a spectral analysis technique (i.e., convolution (equation (2)) in the frequency domain), they found that the shape parameter, α, for the gamma distribution (see Table 2) was approximately 0.5 implying that catchments act as fractal frequency filters at timescales ca. <2 to 3 years. We also tested a simple, less flexible (i.e., one parameter) power law distribution (see Table 2, power law model) and two exponential distributions in parallel (as described by Weiler et al. [2003]).

[22] We used a reflective Newton nonlinear least squares algorithm in MATLAB® to solve the inverse estimation problem of parameter identification for the distributions described above [Coleman and Li, 1994]. We found the set of parameters that minimized the sum of squared residual errors between the modeled and observed stream δ18O. A first-order linear approximation to the parameter variance-covariance matrix (\(\hat{V}\)) is [Donaldson and Schnabel, 1987; Ratkowsky, 1990]:

\[
\hat{V} = s^2(J^TJ)^{-1}
\]  

where \(s^2\) is the estimated residual variance between the model simulation and observations and \(J\) is the Jacobian, which is the matrix of sensitivities of the model output to the parameter estimates. Parameter estimate standard deviations (\(\sigma_p\)) were computed from the square root of the respective diagonal from \(\hat{V}\) [Haggerty et al., 2001]. Approximate 95% confidence limits on parameter estimates were taken as 2\(\sigma_p\). For purposes of model comparison, we used the efficiency (\(E\)) proposed by Nash and Sutcliffe [1970] and the root mean square error (RMSE) corrected for the number of parameters estimated [Bard, 1974]. Other measures such as parameter/objective function scattergrams and temporal sensitivity plots [Knopman and Voss, 1987] were used to evaluate overall model performance but are not directly reported in this paper.

3.4. Topographic Analysis

[23] A 10 m digital elevation model (DEM) was used to compute topographic attributes for each of the 7 seven HJA catchments. Stream networks were determined using a channel-threshold area method. On the basis of observations in several of the small basins, 0.5 ha was used as an initiation area in order to achieve an adequate number of channels at the small basin scale. This threshold area is comparable to other studies in similar topographic systems [Montgomery and Dietrich, 1988; McGlynn and Seibert, 2003]. We used the 0.5 ha threshold for all basins to provide consistency when comparing catchments.

[24] An accumulated area grid was computed using a multidirectional flow algorithm to derive the stream channel network [McGlynn and Seibert, 2003]. Then, a single direction flow algorithm was used to compute flow path length and flow path gradient distributions representing the distance and gradient along each flow line to where it enters the stream network. Likewise, the local subcatchment area for each stream segment (i.e., flagged stream cells) was computed to determine the subcatchment area distribution for each basin [McGlynn and Seibert, 2003; McGlynn et al., 2003]. Since these distributions are typically skewed, we used median values to characterize each basin. Other basic topographic attributes were computed such as the mean slope, hypsometric integral (i.e., the integration of the cumulative frequency distribution of catchment elevations) [Chorley et al., 1985; Strahler, 1952], and topographic index (i.e., \(ln(a/\tan h)\), where \(a\) is upslope accumulated area and \(h\) is the local slope angle) [Beven and Kirkby, 1979]. We then compared these descriptions of internal catchment form at each catchment scale to estimated mean residence times to explore possible relationships (correlation) with catchment topographic organization.

4. Results

4.1. Spatial and Temporal Isotopic Patterns of Precipitation and Streamflow

[25] Precipitation amounts were generally similar between Hi-15 and PRIMET (equal weekly means, \(p = 0.08\)) with slightly more precipitation at the higher-elevation site (Hi-15). The weekly precipitation totals based on the isotope sample collection dates ranged from 0 to 224 mm. Winter (November to April) average weekly amounts were 68 mm and summer (May to Oct.) average weekly amounts were 24 mm. Both sites had significant seasonal patterns of δ18O with approximate annual periodic fluctuations ranging over of 8% for the years 2000 and 2002 (Figure 2). The 2001 period was drier and warmer than average reflecting the more damped isotopic pattern. The Hi-15 isotopic composition, which included snowmelt, was more depleted in 18O than PRIMET, on average by −0.83% (±0.39%).

[26] Spatial variations in rainfall amount and isotopic composition also indicated strong elevation effects (Figure 3). The largest storm sampled spatially (16–17 September) had rainfall amounts that ranged from 19.2 to 75.8 mm (mean = 34 mm). The second and third storms that were sampled were smaller events (mean = 22.9 and 12.2 mm for 29 September to 1 October and 3–5 October, respectively) and had less overall variation (range = 14.7 to 49.1 mm and 5.1 to 18.2 mm for 29 September to 1 October and 3–5 October, respectively). The variation of the storm isotopic composition was −9.7 to −5.6‰, −14.1 to −6.7‰, and −9.5 to −6.9‰, respectively for each storm. Elevation effects for rainfall determined by regression analysis between δ18O and station elevation were −0.24‰ per 100 m (rise in elevation) \(r^2 = 0.64\), −0.26‰ per 100 m \(r^2 = 0.89\), and −0.22‰ per 100 m \(r^2 = 0.84\), respectively for each of the three storms. While only synoptic evidence of strong elevation effects, these data indicated that the input composition for each catchment was temporally unique and therefore required elevation adjustment (equation (1)).

[27] The mean elevation effect between weekly input measurements (rain + snowmelt) at PRIMET and Hi-15 was −0.15‰ per 100 m. This is consistent with values reported in the literature [Clark and Fritz, 1997]. The weekly elevation effect \((S \times 100)\) varied from −1.09‰ per 100 m to 0.78‰ per 100 m, although 90% of the time the values were between −0.22‰ and 0.08‰. Positive
values were typical when the upper elevations were snow covered and melt isotopic composition was muted compared to lower-elevation, cold temperature rainfall (see winter 2001–2002 in Figure 2). Also, cold air drainage, which has a tendency to affect the PRIMET station (C. Daly, personal communication, 2003), could potentially play a role in isotopic fractionation differences between the two monitoring stations, as well as moisture source, rainout history, and rainfall intensity isotopic effects [Ingraham, 1998].

[28] Snowmelt sampled at Hi-15 between 11 December 2001 and 30 April 2002 showed progressive enrichment in $^{18}$O (approximately 0.02% per day for the period 2 January 2002 to 30 April 2002) throughout the melt season (see Figure 2). Snowmelt was not sampled during the 2000–2001 melt season; however, the snowpack was approximately 20% less than the long-term mean. Snowpack persistence at PRIMET rarely exceeded 2 weeks during our study period.

[29] The stream $d^{18}$O composition generally reflected the temporal pattern of the precipitation $d^{18}$O composition; however, the signals were significantly damped (Figures 2). The $d^{18}$O standard deviation for stream water varied from 0.11 to 0.34%, while precipitation standard deviations were 2.98 and 2.80% for PRIMET and Hi-15, respectively. The streams each responded to the early portion of the rainy season and showed an enriched isotopic composition reflective of recent rainfall. Winter periods tended to have a more stable isotopic composition approximately equal to the mean value. However, several sites showed significant variability in winter isotopic signals, which might be related to complex snowmelt processes that were not specifically observed in this study. Mean isotopic composition for each stream is significantly elevation-dependent. The elevation effect between the mean catchment elevations and mean isotopic composition was 0.11% ($r^2 = 0.81; p$ value = 0.006).

4.2. Residence Time Modeling

[30] Most of the residence time distributions (RTDs) provided satisfactory model simulations to the observed isotopic data (i.e., $E$ ranged from 0.2 to 0.6) for all distributions (Table 3). However, only the exponential distribution performed consistently well for all basins (Figure 4). Distributions that contained a mode or did not begin with maximum weighting at the earliest times (e.g., exponential-piston flow distribution and most parameterizations of the dispersion distribution) fit the data poorly (not shown), suggesting that early time rapid response is characteristic of these catchments. Other acceptable distributions for one or several basins included the gamma distribution, two parallel exponential distributions, and power law distribution (see Table 3). The shape parameter, $\alpha$, optimized for the gamma distribution was approximately 1 for all simulations given the large parameter estimate confidence limits. The gamma distribution with $\alpha = 1$ is equivalent to an exponential distribution (see Table 2). The distribution composed of two parallel exponentials provided model simulations with the highest $E$; however, parameters were not identifiable for any of the catchments. The power law distribution did not perform well overall (lowest $E$) (Table 3). It provided simulations with short-term rapid fluctuations and a long-term flat signal that did not represent the nature of the observed isotopic pattern.

[31] The simulations shown in Figure 4 are the best performing exponential models overall. More importantly,
they are among the simplest since only one distribution parameter was optimized (i.e., $t_m$). The model simulations captured the seasonality of the isotopic data very well, especially the early winter rainfall signal. These periods had the greatest influence on the model calibration as indicated by the temporal nature of $t_m$ sensitivity and given that is when the largest isotopic deflection occurs. The mean residence times ranged from 0.8 to 3.3 years with 95% confidence limits (i.e., $2\sigma_p$) of 0.18 to 1.28 years (Table 3).

The relative age differences among these catchments can be shown by the apparent damping of the input isotopic signal in the observed stream water isotopic signal [cf. Maloszewski et al., 1983; Herrmann et al., 1999]. The relationship between $t_m$ and the ratio of the standard deviation of stream water isotopic composition to the standard deviation of precipitation isotopic composition, an indication of signal damping, supported the relative age estimates between the catchments (Figure 5). The Nash-Sutcliffe objective measure ranged from 0.32 to 0.54 for the exponential model simulations.

The effective recharge elevations for each catchment were optimized to obtain mass balance between the stream isotopic composition and the input composition given by equation (1). Only WS02, WS03, MACK, and LOOK basins had effective recharge elevations that were higher than the reference precipitation station elevation. Thus only these catchments had significant input isotopic elevation

<table>
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<th>Table 3. Residence Time Modeling Results$^a$</th>
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$^a$The best fit parameter value, its associated 95% confidence limits (i.e., $2\sigma$), measure of efficiency ($E$), and root mean square error (RMSE) are listed for each model.

$^b$Estimated recharge elevation ($E_R$). Values are only reported for the exponential model since estimates for all other models were similar. Note that $E_R$ estimates for WS08, WS09, and WS10 were not significantly different than their minimum catchment elevation (Table 1); thus the $\delta^{18}O$ in precipitation did not have an elevation effect.

$^c$If estimates of the confidence limits are not shown, they were >5 times the parameter estimate; thus the given parameter estimate was ill determined.
effects. The remaining catchments (WS08, WS09, and WS10) had effective recharge elevations equal to the elevations of the precipitation collection stations. Effective recharge elevations for WS02, WS03, MACK, and LOOK were between 20 and 40% of the catchment elevation range (647 m, 594 m, 1010 m, and 916 m for WS02, WS03, MACK, and LOOK, respectively). No differences were observed in calibrated effective recharge elevations when other residence time models were used. The effective recharge elevation parameter only changes the input composition to reflect the observed isotopic elevation effects (Figure 2).

[33] The RTDs in Figure 6 illustrate the diverse transport behavior within the overall LOOK drainage. These distributions indicate the relative memory of the catchments to past inputs and thus reflect how long these catchment store and release water or conservative contaminants. The distributions for WS09 and WS10 are more responsive than the other basins, which release between 35% and 42% of the total stored water annually, compared to 70% and 56% for WS09 and WS10, respectively. Not surprisingly, catchments with similar geology/geomorphology had similar RTDs (Table 1).

[34] Since several of the distributions have rather prolonged residence times, the length of the input function must be considered to assess uncertainty. The amount of tracer mass that would pass through these catchments over the timeframe given by the measured portion of the input function (1131 days) is one way to assess the uncertainty of the distribution (shown in Figure 6 where the distribution curves become dashed lines). Therefore, if 100% of the tracer mass exists within the timeframe of the input measurement, then one would have more confidence in the selection of that RTD. The recovered mass at 1131 days was 75, 81, 61, 98, 92, 79, and 78% for WS02, WS03, WS08, WS09, WS10, MACK, and LOOK, respectively. We argue that in addition to parameter estimation error ($\sigma_p$), these recovery rates indicate uncertainty caused from the dependence on the extended input data (see section 3.2). For example, 39% of the tracer mass in WS08 originated prior to our observations. Cumulative residence time distributions shown in the inset of Figure 6 further illustrate this point.

4.3. Residence Time and Topographic Analysis

[35] Catchment area showed no apparent relationship to the estimated mean residence times ($\tau_m$) ($r^2 < 0.01$) (Figure 7a). The two largest basin scales, MACK (5.81 km²) and LOOK (62.42 km²), had younger $\tau_m$ than WS02 (0.601 km²) and WS08 (0.214 km²), while catchments with the youngest $\tau_m$ were the smallest basins (WS09 and WS10, 0.085 and 0.102 km², respectively). Other topographic indices were regressed against the mean residence time, including the accumulation of subcatchment areas (e.g., median subcatchment area, $r^2 < 0.01$), the hypsometric integral ($r^2 = 0.36$, $p = 0.213$), and the mean topographic index ($r^2 = 0.85$, $p < 0.01$). Mean values of the topographic index did not vary significantly between catchments (6.1 to 7.2). Topographic characteristics that described surface flow path attributes were highly correlated to $\tau_m$ (see Figure 7; note that WS09 was not included in most of the topographic analyses because the DEM resolution was not sufficient to define the stream channels; however, it was expected to behave similarly to WS10). Even simple measures such as the catchment average slope showed significant correlations with $\tau_m$ ($r^2 = 0.78$, $p < 0.01$).

[36] Distributions of flow path lengths and gradients computed from the DEMs provided information regarding the internal arrangement of flow pathways and area accumulation, which are thought to control transport at the gross catchment scale. Figures 7b, 7c, and 7d show the medians of flow path length ($r^2 = 0.72$, $p = 0.03$), flow path gradient ($r^2 = 0.64$, $p = 0.056$), and their ratio (LG ratio) ($r^2 = 0.66$, $p = 0.004$). The distributions for WS09 and WS10 are more responsive than the other basins, which release between 35% and 42% of the total stored water annually, compared to 70% and 56% for WS09 and WS10, respectively. Not surprisingly, catchments with similar geology/geomorphology had similar RTDs (Table 1).
In other words, the overall basin residence time represents an integration of the various subbasin residence times. However, the confidence limits (Table 3) indicate that \( \alpha \) was not well identified.

The high variability contained in the stream isotopic data for several of our sites (e.g., WS02, WS08, and LOOK) suggests that more complex processes occur in these basins that cannot be represented in simple lumped parameter models. Nevertheless, these models capture the dominant isotopic pattern over a large range of spatial scales where there is extreme variability in runoff generation and snowmelt processes. Haitjema [1995] suggests that the exponential distribution as obtained by assuming steady state Dupuit-Forchheimer flow is independent of catchment size, shape, stream network, and hydraulic conductivity distribution, as long as the saturated zone remains relatively constant. Our analyses seem to support the exponential distribution as a first-order approximation to the true RTD. However, given the extremely damped output \( \delta^{18}O \) signal of all sites, rigorous discrimination between models was not possible. Differences in the observed degree of isotopic damping between sites strongly suggest that the relative residence time differences between basins were approximately correct (Figure 5).

Similar model fits have been obtained by other investigators using lumped parameter isotope models [Maloszewski et al., 1992; Vitvar and Balderer, 1997; Uhlenbrook et al., 2002; McGuire et al., 2002]. While one can argue that more complex models are warranted for catchment systems, uncertainty in the input composition and parameter estimation of more complex RTDs suggests that models with the fewest degrees of freedom are more practicable [Maloszewski and Zuber, 1993, 1998].

5. Discussion

5.1. Residence Time Modeling

The mean and distribution of residence times estimated in this study using stable isotope tracers are not unlike results (1–5 years) found for other small basin (<100 km³) studies [Maloszewski et al., 1983; Lindström and Rodhe, 1986; Maloszewski et al., 1992; Rodhe et al., 1996; Vitvar and Balderer, 1997; Burns et al., 1998; Herrmann et al., 1999; McGuire et al., 2002; Uhlenbrook et al., 2002]. However, these studies evaluated residence time for only 1 to 3 catchment scales, as opposed to our investigation that included 7 catchment scales with mean residence time estimates ranging from 0.8 to 3.3 years for basins between 0.085 and 62.42 km² in a diverse geomorphic setting. Residence time does not depend on catchment scale. The largest catchment, LOOK, has a residence time that was intermediate to the other basins indicating that its dominant flow sources represent some average contribution of sources that are contained within the other basins. In other words, the overall basin residence time represents an integration of the various subbasin residence times.

The exponential distribution that we used in our residence time modeling represents the simplest possible distribution given that there is only one parameter to estimate for the distribution. Other distributions, while more flexible due to a larger number of parameters, often produced better model simulations (i.e., larger \( E \)), but we could not justify using more complex distributions since all or some of the parameters were not identifiable (Table 3). In addition, gamma distributions parameterized to fit these observations were essentially exponential, indicating the exponential distribution of residence times is a good, reasonable approximation given the input-output isotopic data available. The estimated shape parameter (\( \alpha \)) for several of the catchments (WS02, WS03, and WS10) was less than 1 suggesting these approach the fractal scaling observed by Kirchner et al. [2000]. However, the confidence limits (Table 3) indicate that \( \alpha \) was not well identified.

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5.2. Topographic Relationship

Results from some studies [Fritz, 1981; Burgman et al., 1987; DeWalle et al., 1997; McDonnell et al., 1999; Soulsby et al., 2000] have implied that there is a positive correlation between basin area and residence time; however, as shown in this study and other recent studies [McGuire et al., 2002; McGlynn et al., 2003; Rodgers et al., 2005], basin area does not seem to be related to residence time. The strong correlation between mean residence time and simple terrain indices found here suggests that the internal topographic arrangement, as opposed to basin area, may control catchment-scale transport. These results are in contrast to other studies such as that by Wolock et al. [1997], who suggested that the spatial pattern of low-flow stream chemistry across basin scale was systematically related to an increase in subsurface contact time (a residence time surrogate) and basin scale. We do not find a consistent relationship between basin scale and residence time in our study.
In areas with significant relief, the flow path distribution at the catchment scale is expected to follow the general topographic form of the basin. The catchment-scale flow path distribution is largely a function of catchment geometry [Kirchner et al., 2001; Lindgren et al., 2004], the spatially variable contributing areas [McDonnell et al., 1991], and expression of groundwater seepage [Asano et al., 2002]. At the hillslope scale, residence time should increase with accumulated area or flow path length as was observed by Stewart and McDonnell [1991] and Rodhe et al. [1996]. Asano et al. [2002] tested this hypothesis and found that residence time increased only with accumulated area for perennial shallow groundwater defined by bedrock seeps and that transient shallow groundwater in the soil profile appeared to age in a vertical direction (i.e., dependent on soil depth). These studies suggest that even at the hillslope scale, the flow path distribution is quite complex. However, as one moves to the catchment scale, a clear pattern emerges, where residence times increase with flow path length (i.e., catchment geometry) and decrease with flow path gradient (Figure 7). Butt et al. [2001] and Rodhe et al. [1996] both found weak correlations between groundwater residence times in various catchment positions and the \(\ln(a/tan^3)\) index, suggesting similar behavior. Interestingly, the correlation of residence time with \(L/G\) is significantly better than the correlation of residence time with flow path length \(L\) or flow path gradient \(G\) individually. This suggests that both factors are important controls on residence time.

The relationship between the accumulation of contributing areas and residence time was explored by McGlynn et al. [2003]. They found that the mean residence time estimated from tritium data was positively correlated to the median area of all subcatchments that drain to the stream (i.e., dependent on mean discharge). For example, based on the estimated \(\tau_m\) for WS10 (1.2 years) and the average annual runoff (1480 mm/y), one would expect approximately 1776 mm of storage. Since soil depths on average for WS10 are between 1 and 3 m and effective porosity \(\approx 0.2\) [Ranken, 1974], then the storage would exceed the capacity of the soil, suggesting that bedrock storage is significant, but still topographically controlled. Similar interpretation can be made for the other HJA catchments, indicating that while topography controls flow, storage in bedrock is significant.

The lack of relationship between basin area and \(\tau_m\) may indicate differences in the geology and geologic history of the landscape. Average basin slope explains 78% of the variance in \(\tau_m\), indicating that it was one of the most important topographic factors in our study. The average slope is also highly correlated to the logarithm of basin area \((r^2 = 0.94, p < 0.01)\). If WS08 is removed as an outlier, this suggests indirectly, that \(\tau_m\) is related to basin area provided that geology is generally consistent across basins. In the HJA, lower-elevation basins (WS02, WS03, WS09, WS10) are mostly underlain by the highly weathered Oligocene–lower Miocene volcaniclastic rocks. The topography in these areas is characterized by steeply dissected short hillslopes. Many of the upper elevation small basins in the HJA have been glaciated and/or contain earth flows and thus have gentle topography and longer hillslopes. While our data set is limited to only one catchment in this geologic type (i.e., WS08), these basins do not conform to the log linear relationship between basin slope and area. Therefore correlation between basin area and \(\tau_m\) may be obscured by geologic differences among basins. Other topographic measures presented herein (e.g., \(L/G\) ratio) may reflect these geologic features more directly.

5.3. Beyond Small Catchments

Empirical results from this study suggest that the internal form and structure of the basin defines a fundamental control on the catchment-scale residence time. Indeed more multiscale studies focused on residence time and other measures that integrate processes at the catchment scale are necessary to verify relationships such as those presented in this study. However, relationships between topographic measures that can be easily computed from DEMs and residence time may provide a way to regionalize process descriptions of catchments to scales of interest for management, modeling, and biogeochemical studies. Information gathered from intense tracer studies at a limited number of diverse end-member catchments, might be extended to characterize larger systems (i.e., upscaling) or facilitate a more complete understanding of mesoscale systems where measurements that differentiate processes are difficult to obtain [Uhlenbrook et al., 2004; Soulsby et al., 2004].

The RTD is a fundamental descriptor of catchment hydrology. Knowledge of residence time has important implications to how one might define models at the mesoscale where data are limited. In this study, the estimated mean residence times indicate that there is a landscape-level
organization (i.e., topography), which can be used to distribute information regarding average storage or flow velocity. This information can then be used in a priori model development and/or multicriteria model calibration [Melhorn and Leibundgut, 1999; Uhlenbrook et al., 2000]. Furthermore, the RTD provides an integrative measure and process description of hillslope complexity at the catchment scale that may be used to infer model structures and advance their predictive capability [Sivapalan, 2003].

6. Conclusions

Although residence time has been implicated in other studies to scale with catchment area, this study has shown that the internal form and structure of the catchment, as opposed to absolute catchment area, controls catchment-scale transport. Seemingly simple topographic attributes such as the median flow path length and gradient, which can be computed from any digital elevation model, were strongly correlated to residence time distributions at the catchment scale that represent relatively complex hydrological processes. This relationship allows for the regionalization of residence time and insight to process understanding at the mesoscale. Results from this study suggest that tracers might help bridge the gap between small basins and the mesoscale by providing a linkage between topography, scale, and process. Furthermore, approaches such as the one presented here, provide opportunities to investigate patterns and processes across scale and to offer new perspectives into hydrological and hydrochemical processes that may only become apparent at larger scales.

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