

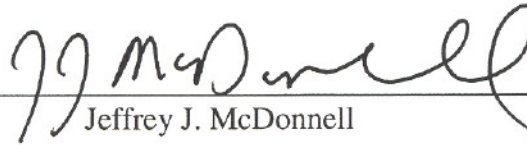
## AN ABSTRACT OF THE DISSERTATION OF

Kevin J. McGuire for the degree of Doctor of Philosophy in Forest Engineering presented on September 30, 2004.

Title: Water Residence Time and Runoff Generation in the Western Cascades of Oregon.

Abstract approved:

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Jeffrey J. McDonnell

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 to characterize catchments, there are few studies that quantify residence time at the catchment scale or explore the process controls on the distribution of residence times. The objective of this study is to determine the controls on catchment-scale residence time using hydrometric, tracer, and modeling approaches at hillslope to multiple catchment scales. Topographic controls on residence time are examined for seven catchments at the H. J. Andrews Experimental Forest that range in basin area from 0.085 to 62.4 km<sup>2</sup> representing diverse geologic and geomorphic conditions. Residence times are estimated using stable isotope tracers and convolution integral models. Baseflow mean residence time results range from 0.8 to 3.3 years. There is no correlation between residence time and basin area; however, mean residence time is correlated to the catchment-scale median flowpath distance and flowpath gradient to the stream network, suggesting that topography is a first-order control on catchment-scale transport. The examination of detailed hydrological processes at the hillslope scale through a wet-up period, provide the basis for a dynamic conceptual model of runoff generation and residence time, which are

controlled by moisture thresholds and expanding subsurface saturated areas. The residence time of runoff during storms is a dynamic amalgamation of various components, each with their own characteristic shape, mixing behavior, and timescale, which range from 6 to 27 hours for event water and 10 to 30 days for soil water. A coupled hydrologic-tracer model at the hillslope scale indicates that the combination of storm event and between-event processes is necessary for the representation of realistic residence time distributions at hillslope and catchment scales. This study demonstrates that water residence time provides insight to hydrological processes from hillslope to large catchment scales.

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Water Residence Time and Runoff Generation in the Western Cascades of Oregon

by  
Kevin J. McGuire

A DISSERTATION

submitted to  
Oregon State University

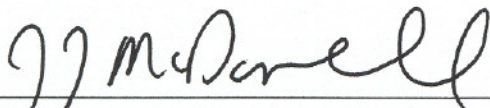
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degree of

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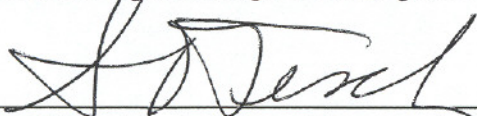
Presented September 30, 2004  
Commencement June 2005

Doctor of Philosophy dissertation of Kevin J. McGuire presented on September 30, 2004.

APPROVED:



Major Professor, representing Forest Engineering

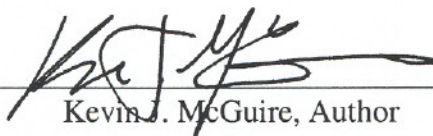


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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.



Kevin J. McGuire, Author

## ACKNOWLEDGEMENTS

I am most grateful to my wife, Dana, whose constant companionship and emphatic encouragement made this work possible. I appreciate her willingness to move to the opposite side of country from family and support me during these last four years. I also thank my parents, Carol and Jim, as well as Kathy and Al Friedman for their continual support and love.

I would like to express my sincere thanks and appreciation to my advisor and mentor Jeff McDonnell for always being so positive and encouraging. His infectious enthusiasm has been an endless source of inspiration and motivation through my Ph.D. program. I am deeply grateful for his guidance and support.

I also would like to thank my committee members Arne Skaugset, Julia Jones, Roy Haggerty, and Jim Reeb for insightful discussion and helpful comments. I also recognize and thank Sherri Johnson, Fred Swanson, and John Cissel for many candid and open discussions on HJA and Pacific Northwest science. I am indebted to John Moreau, Craig Creel, Greg Downing, and Terry Cryer who generously donated their time and expertise with field assistance and helped with sample collection. I am genuinely grateful for the field and lab assistance provided by Brett Morrisette during the storm season. I thank Don Henshaw for help with HJA data access. I would like express my gratitude to both Charlie Luce and Paul Schuster for providing water chemistry analyses and Rick Hooper for his involvement and advice. Carol Kendall provided isotope analysis on many water samples, without which, this dissertation would not have been possible. I truly value her support and collaboration.

A special thanks to Ilja Tromp-van Meerveld, Markus Weiler, Willem van Verseveld, Kellie Vaché, Brian McGlynn, Nick Hjerdt, Richard Keim, Jan Seibert, Taro Uchida, and Tomas Vítvar, and Derek Godwin. I consider myself extremely lucky to have had the opportunity to interact with all of you on a daily basis. I value your friendship and have the utmost respect for you as colleagues. I especially thank Markus Weiler for serving as an unrecognized, informal second advisor and good friend.

I also truly enjoyed discussions with Yuko Asano, Hannah Cloke, Stefan Uhlenbrook, Corinna Starcke and especially Stephen Sebestyen during extended visits to our lab. Stephen's assistance during the summer and fall of 2001 was invaluable to this project and so were the many scientific discussions held on the WS10 hillslope.

Financial support for my graduate program was provided by the Department of Forest Engineering and other financial assistance throughout my program was provided by the HJA LTER program.

## CONTRIBUTION OF AUTHORS

Several authors were involved in Chapter 3. Markus Weiler assisted with the residence time modeling, Brian McGlynn and Jan Seibert helped with the topographic analysis, and Carol Kendall and Jeff Welker provided isotopic analysis.

Carol Kendall provided isotopic analysis for Chapter 4.

Markus Weiler assisted with conceptual development and modeling of Chapter 5.



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## **1 Introduction**



## 1.1 Introduction

Thirty years after the International Hydrological Decade (IHD) [Nace, 1980], and at the beginning of a second international hydrological decade focused on Prediction in Ungauged Basins [Sivapalan *et al.*, 2003], hydrologists still struggle with the fundamental question of how long water resides in the subsurface. This seemingly simple question often belies hydrological description due to the complexity and heterogeneity of catchment flow paths [Anderson and Burt, 1990; Bonell, 1993, 1998]. We still do not know how to distill the complex hydrological processes of catchments into parsimonious models that can be used for prediction, learning, and extrapolation. While models of water quantity do not necessarily need detailed process descriptions to simulate runoff [e.g., Jakeman and Hornberger, 1993; Young, 2003], water quality models that are used to simulate weathering rates, nutrient cycling, solute transport, or contaminant transport, require a more process-oriented description of runoff generation where the water residence time is highly relevant. Catchment hydrology is changing from a calibration-based modeling paradigm (i.e., fitting models to discharge data) to a new paradigm where model parameters are consistent with process descriptions and internal catchment data [Sivapalan, 2003]. Recent studies have begun to incorporate new measures of model performance (e.g., groundwater levels, chemistry, and soil moisture) to evaluate if models are working for the right reasons and are consistent with internal catchment data [Kuczera and Mroczkowski, 1998; Seibert and McDonnell, 2002; Wagener, 2003; Freer *et al.*, 2004].

Over the past 20 years, environmental tracers, such as the stable isotopes of water ( $^{18}\text{O}$  and  $^2\text{H}$ ), have provided insights into hydrological processes; from definition of

groundwater and surface water age, to hydrograph source components, to descriptions of water flow pathways at the catchment scale [*Sklash*, 1990; *Buttle*, 1994; *Kendall and McDonnell*, 1998]. Environmental tracers serve as natural experiments at large-scales. Through interpretative models, environmental tracers can provide estimates of catchment-scale properties not obtainable through point and plot-scale hydrometric measurements (e.g., catchment-scale subsurface flow rates). Nevertheless, tracer methods have also indicated that complex and unique processes range across scale and vary among catchments [e.g., *Sklash and Farvolden*, 1979; *Eshleman et al.*, 1993; *Peters et al.*, 1995; *McDonnell*, 1990]. These results suggest the need for a hydrological concept that is scaleable and that connects internal/hillslope process complexity to catchment-scale simplification [*Sivapalan*, 2003]. In the chapters that follow, the residence time distribution of catchments is shown to possess these attributes.

The catchment residence time distribution, which is determined primarily using environmental tracers, describes conceptually the integration of the catchment flow pathways, storages, transport velocities, and hillslope and catchment morphologies. Quantifying the residence time distribution is essential for many water quality applications, for example, to predict the fate and transport of fertilizer and herbicide treatments [e.g., *Landon et al.*, 2000; *Spurlock et al.*, 2000], and the catchment response time to land-use and environmental change, including forest harvest [e.g., *Reeves and Rosen*, 2002; *Buttle et al.*, 2001]. Residence time offers a link to water quality, since the contact time within the subsurface largely controls the natural stream chemical composition, time-dependent biogeochemical reactions, and persistence of contaminants [*Burns et al.*, 1998; 2003; *Kirchner et al.*, 2000; *Hornberger et al.*, 2001]. Furthermore,

residence time can be used to constrain, reject, or validate catchment model structures in order to remain consistent with process descriptions [*Vaché et al.*, in press] and develop better predictions of water, solute, and nutrient flux at the catchment scale.

*McGlynn et al.* [2003] recently tested the scalability of mean residence time estimated using environmental tracers. Although their work showed that the mean residence time did not scale with catchment size, it suggested that landscape organization, reflected by the pattern of catchment area accumulation, controlled catchment-scale mean residence time. This is an important finding since transferring information from one scale to another remains perhaps the greatest challenge in hydrology today [*Beven and Fisher*, 1996; *Rosgen*, 1999; *Bergström and Graham*, 1999; *Sivapalan et al.*, 2004]. Scaling research in general has been lacking in empirical data and process-level information to adequately develop relationships between scales and hydrological processes [*Blöschl*, 2001]. As shown by *McGlynn et al.* [2003], residence time may offer an ability to extend process information across scale.

## **1.2 Chapter Descriptions**

The research described in the following chapters is aimed at illuminating the “black-box” of catchments and providing improved methods for estimating the catchment-scale residence time distribution and understanding its physical controls. Each chapter builds on previous chapters within the overall theme of residence time and runoff generation. This work focuses on catchments in H.J. Andrews Experimental Forest (HJA), which is located in the west, central Cascade Mountains of Oregon, USA and is part of the Long-Term Ecological Research program of the National Science Foundation.

Chapter 2 introduces the residence time estimation approach through an evaluation and review of residence time studies in catchments. In general, residence time estimation at the catchment-scale (i.e., time required for all water travel to the basin outlet) is based largely on simple lumped parameter models developed in the groundwater and chemical engineering disciplines. In chapter 2, after describing basic theory and methods, I attempt to expose the assumptions and limitations that are most critical in applying lumped parameter residence models to catchments. Six issues that relate to measurements, modeling, and interpretation associated with catchment residence time are identified and discussed:

- The input characterization issue
- The recharge assumption
- The data record length problem
- The stream sampling issue
- The residence time distribution selection problem
- The model evaluation process

As these issues are discussed, recommendations derived from recently published studies and new research presented herein, provide a guideline for future research and application of lumped parameter residence time modeling at the catchment scale.

Chapter 3 examines how residence time varies across catchment scale. Topographic attributes are examined within a regionalization framework and as potential controls on catchment-scale residence time. This study builds upon the findings of *McGlynn et al.* [2003] in a suite of catchments from the HJA that exhibit large geomorphic and climatic variation. The goal of the study is to understand the linkages

between residence time and landscape features based on empirical evidence. The study presented in chapter 3 has important implications for meso-scale (10's to 100's of km<sup>2</sup>) hydrologic modeling, since there is a general lack of data to conceptualize or parameterize these models. The regionalization of residence time results offers the ability to constrain model representations of storage (or flushing rates) and flow pathways across scale and in a landscape (meso-scale) context. Hydrologic models at these scales are needed to match management plans that are being developed at the landscape level by various government and state agencies [e.g., *Bowling et al.*, 2000; *Alila and Beckers*, 2002].

Chapters 4 and 5 focus on deconvolving the complexity of runoff processes at the small catchment and hillslope scales with the purpose of discerning the dominant controls on runoff generation and the distribution of residence times. Motivation for chapter 4 is to understand how the connection between hillslopes and catchments varies through different wetness conditions. The activation of hillslope connectivity (i.e., when hillslopes become hydrologically connected to the stream and/or with other regions in hillslope) often coincides with the flushing of liable nutrients, which has important implications for receiving waters in aquatic ecosystems and for general nutrient cycling processes [e.g., *Creed et al.*, 1996]. Measurements of hydrometric data (soil moisture, groundwater levels, hillslope seepage, and catchment runoff) are made and stable isotope tracer and applied hillslope tracer data are collected through a wet-up phase of the WS10 catchment in the HJA. These data are used to estimate the residence time of runoff components and to establish a general conceptual model for the dominant runoff generation processes. Four null hypotheses are tested:

- Stream discharge is linearly related to hillslope discharge
- Hillslopes are not capable of transporting solutes (tracer) to the stream from upslope areas during a storm event
- Event water contributions are similar for the hillslope and catchment
- Hillslope residence time increases downslope and is similar to the stream when it reaches the slope base.

Chapter 5 presents the application of a simple, spatially-explicit hillslope model to an applied tracer experiment. The objectives of this chapter are to integrate a modeling approach with an applied tracer study to simplify observed process complexity, evaluate model performance, and explore process controls on potential hillslope residence time distributions. The tracer data, combined with an historical soil hydrologic dataset, are used to constrain the model parameter range and meet the objectives above. The coupling of solute tracer and hydrologic models allows for a comprehensive evaluation of model structure, in terms of predicting runoff and tracer, and verification that the model is working for the right reasons [*Klemeš*, 1986; *Wagener*, 2003].

The final chapter (chapter 6) provides a summary and conclusion for the overall dissertation. Areas of future work are identified. Overall, the chapters in this dissertation represent a combined hydrometric, tracer, and modeling approach at various scales from hillslope, to small and large catchments, for the investigation of water residence time and runoff generation at the catchment scale.

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## **2 A review and evaluation of catchment residence time modeling**

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## 2.1 Introduction

The time water spends traveling through a catchment (i.e., the residence time) is a fundamental catchment descriptor that reveals information about the storage, flow pathways and source of water in a single characteristic. Residence time is a physical measure that transcends catchment scale, is easily scaleable [Sivapalan, 2003], and is directly related to internal catchment processes [Stewart and McDonnell, 1991]. The residence time describes how catchments retain and release water and solutes that in turn control geochemical and biogeochemical cycling and contamination persistence. Longer residence times indicate greater contact time and subsurface storage implying more time for biogeochemical reactions to occur as rainfall inputs are transported through catchments toward the stream channel [Scanlon *et al.*, 2001; Burns *et al.*, 2003]. Thus, quantifying the residence time and, more importantly the residence time distribution, provides a primary description of the hydrobiogeochemical system [Wolock *et al.*, 1997] and catchment sensitivity to anthropogenic inputs [Nyström, 1985; Landon *et al.*, 2000] and land-use change [e.g., Buttle *et al.*, 2001]. Despite the importance of residence time and its distribution, it is impractical to determine experimentally except in rare manipulative experiments where catchment inputs can be adequately controlled [cf. Rodhe *et al.*, 1996]. Thus, residence times are usually inferred using lumped parameter models that describe integrated transport of tracer through a catchment. These models do not require detailed hydrological characterization of the physical system and, consequently, are often used for characterizing catchments in less developed countries and ungauged basins.

There has been considerable interest recently in residence time as new river monitoring programs develop [e.g., *Gibson et al.*, 2002; *Aggarwal*, 2002; *Hooper*, 2004] to quantify stores and fluxes of water in large catchment systems (up to 10,000 km<sup>2</sup>). There are readily available computer codes that are used to interpret environmental tracer data to estimate residence time using the standard lumped parameter models [*Richter et al.*, 1993; *Maloszewski and Zuber*, 1996; *Bayari*, 2002; *Ozyurt and Bayari*, 2003]. However, there is little guidance on the assumptions and limitations of different modeling approaches applied to catchment systems. Even more problematic is the lack of guidance on how to quantify model uncertainty of residence time estimates and identifiability of parameters used in the models. We would argue that while there have been numerous recent publications (references provided herein and Table 2.1) using tracers to estimate residence times, relatively little advancement in residence time estimation methodology has been made at the catchment-scale. Most methods are based on early adaptations from the chemical engineering and groundwater fields [e.g., *Danckwerts*, 1953; *Eriksson*, 1958; *Maloszewski and Zuber*, 1982; *Haas et al.*, 1997; *Levenspiel*, 1999] and may not apply in catchments where there are complex and important controlling processes like variable flow in space and time, spatially variable transmissivity, coupled vertical and lateral flow, immobile zones, and preferential flow, to name a few. Very little guidance exists for catchment hydrologists on the use and interpretation of residence time modeling approaches for complex catchment systems.

The catchment-scale lumped parameter models that exist for the interpretation of tracer input (i.e., precipitation) and output (i.e., streamflow) data assume that the hydrologic system is at steady-state and that representative inputs can be determined

[*Maloszewski and Zuber, 1996*]. In catchments, these assumptions are almost always violated. Techniques have been developed to estimate residence time for non-steady (variable flow) systems [*Lewis and Nir, 1978; Niemi, 1978; Zuber, 1986; Rodhe et al., 1996*]; however, they are rarely used in the published literature owing to their complexity and the difficulty in interpreting results. Characterizing representative inputs for catchments can be problematic considering that precipitation is highly variable in space and time for tracer composition and precipitation amount. Catchments receive inputs that are distributed over all or part of their area, which are then transported along flow pathways that represent the full spectrum of possible pathways to the stream network. This complex 3-dimensional problem is typically simplified so that parameters that describe the flow system can be estimated. These simplifications include 1-dimensional transport, time-invariant residence time distributions, and uniform recharge [*Turner and Barnes, 1998*]. These simplifications may lead to uncertainty in residence time characterization; nevertheless, this has not been critically evaluated in the literature, especially in the context of catchments.

While some of these problems have been recently addressed in benchmark reviews by *Maloszewski and Zuber* [1993; 1996] and *Zuber and Maloszewski* [2000], their work has focused on using environmental tracers to estimate the residence time of groundwater systems. The treatment of stable isotope techniques has been absent in several reviews concerning residence time [e.g., *Plummer et al., 1993; Cook and Böhlke, 2000*], even though stable isotopes are the main tracers available for determining residence times of stream/catchment systems and young groundwater (i.e., <5 years old) [e.g., *Moser, 1980; Coplen, 1993; Clark and Fritz, 1997; Turner and Barnes, 1998;*

*Coplen et al.*, 2000]. We contend that problems, limitations, assumptions, and methods have not been clearly evaluated and synthesized for residence time model applications in catchments. In this review, we provide an overview of the methods available to estimate catchment-scale residence time and present a formal listing of the sampling, modeling, and interpretation issues concerning residence time estimation in catchments. We begin with an overview of the basic concepts and modeling theory, and then introduce and address six assumptions and problems that arise from estimating residence time using lumped parameter models.

## **2.2 Basic Concepts**

We focus our discussion of residence time estimation in streams on the use of environmental tracers of the water molecule itself,  $^{18}\text{O}$ ,  $^2\text{H}$ , and  $^3\text{H}$ . These ideal tracers are applied by precipitation and are generally distinct isotopically, which makes them reliable tracers of subsurface flow processes [*Kendall and Caldwell*, 1998]. While groundwater residence times are estimated using dissolved gas environmental tracers (namely chlorofluorocarbons (CFCs), tritium/helium-3 ( $^3\text{H}/^3\text{He}$ ), sulfur hexafluoride ( $\text{SF}_6$ ), and krypton-85 ( $^{85}\text{Kr}$ ) [*Ekurzel et al.*, 1994; *Cook and Solomon*, 1997; *Solomon et al.*, 1998]), these tracers are not applicable to stream waters because of contamination by exchange with atmospheric and vadoze zone gases [*Cook and Solomon*, 1995; *Plummer et al.*, 2001].

Stream water is an integrated mixture of water sources with an age (or residence time) that reflects the ages of all rainfall that fell on the catchment in the past. At any point along a flow path in a catchment, the residence time would be defined as the time

that has past since a water molecule entered the catchment [*Maloszewski and Zuber, 1982*]. Some distinction has been made in the past between the definitions of age (or residence time) and transit time, [*Bolin and Rodhe, 1973; Etcheverry and Perrochet, 2000*]. The residence time is the time that has elapsed since the water molecule(s) entered the catchment, whereas when the water molecule(s) exits the catchment (at the basin outlet), it is called the transit time. For the purposes of this paper, we consider their meanings to be synonymous because the point of measurement is typically the catchment outlet. Also, tracers are assumed to be conservative, measured in flux mode [see *Kreft and Zuber, 1978*], and enter/exit the catchment only once.

First, we consider a simple water balance, the hydraulic turnover time,  $T$ , is defined as:

$$T = S/Q \quad (1)$$

where  $S$  is the mobile catchment storage ( $L^3$ ) and  $Q$  is the volumetric flow rate ( $L^3 T^{-1}$ ) that is assumed to be constant or an average value. From Darcy's law,  $T$  can be expressed as [*Mazor and Nativ, 1992*]:

$$T = n_e (\Delta l)^2 / K \Delta h \quad (2)$$

where  $\Delta l$  is the distance from recharge to discharge (L),  $\Delta h$  is the difference in hydraulic head over the distance  $\Delta l$  (L),  $n_e$  is the average effective porosity ( $L^3 L^{-3}$ ), and  $K$  is the average hydraulic conductivity over the distance  $\Delta l$  ( $L T^{-1}$ ). This  $T$  is often the point of reference for residence times, since it defines the turnover timescale based on our best understanding or assumption of the catchment subsurface volume and mobile storage.

The residence time distribution (RTD) can be represented as the response or breakthrough of an instantaneous, conservative tracer addition over the entire catchment area:

$$g(t) = \frac{C_I(t)}{\int_0^{\infty} C_I(t) dt} = C_I Q / M \quad (3)$$

where  $C_I(t)$  is the instantaneous concentration of tracer at  $t=0$  ( $M L^{-3}$ ) and  $M$  is the injected mass ( $M$ ). The RTD (or  $g$ ) describes the fractional weighting of when mass (i.e., tracer) exits the catchment, which is equivalent to the probability density of tracer leaving the catchment resulting from the tracer applied instantaneously to the entire surface of a catchment. The RTD must sum to unity in order to conserve mass and it represents all possible flow pathways in a hydrological system. Other common terms for the RTD are the transit time distribution, tracer age distribution, system response function, age spectra, first passage time, and weighting function. The mean residence time of the tracer ( $\tau_m$ ) is simply the first normalized moment or the average arrival time of  $C_I(t)$  at the catchment outlet:

$$\tau_m = \int_0^{\infty} t C_I(t) dt \bigg/ \int_0^{\infty} C_I(t) dt = \int_0^{\infty} t g(t) dt \quad (4)$$

It has become common to estimate the mean residence time, since it can be compared to the hydraulic turnover of a catchment (Eqn. 1). However, RTDs are typically skewed distributions with long residence time tails; thus, other moments (variance, skewness, etc.) and central tendency values (i.e., median and mode) are often more suitable to describe the shape and scale of the distribution.



Although these definitions (Eqns. 3 and 4) seem highly theoretical, given that we do not ever have such an experiment at the catchment scale,  $g$  represents conceptually the response of the catchment to a unit tracer input and is analogous to a unit hydrograph for tracer. It is therefore useful to predict the tracer composition of stream flow assuming that the function  $g(t)$  is known or approximately characterizes the flow system.

*Mazor and Nativ* [1992] claim that comparing the residence time and turnover time is often more instructive than estimating only one or the other, since they can describe different aspects of the subsurface system. For example, the residence time describes the entire volume of subsurface water that contributes to runoff, whereas the turnover time describes the dynamic or mobile volume. If the tracer is conservative and there are no stagnant zones in the catchment, then the mean residence time of the tracer will equal the mean residence time of the water ( $\tau_m = T$ ). *Mazor and Nativ* [1992] discuss other examples that yield differences between  $\tau_m$  and  $T$  in aquifer systems, which mainly relate to poor characterization of the extent and nature of the subsurface flow system. Essentially, the volume of the subsurface that tracer can access is typically larger than that determined based on hydraulic relationships alone [e.g., *Bergmann et al.*, 1986; *Melhorn and Leibundgut*, 1999; *Vitvar et al.*, 2002], since it is difficult to characterize hydraulic discontinuities or groundwater entrapment in immobile volumes [*Mazor and Nativ*, 1992].

### **2.3 Residence Time Modeling Theory**

Water residence time distributions for catchments can be determined experimentally from temporal variations of stable isotopes ( $^2\text{H}$  and  $^{18}\text{O}$ ), tritium ( $^3\text{H}$ ), and

other conservative tracers (e.g., chloride) [Dinçer *et al.*, 1970; Maloszewski and Zuber, 1982; Pearce *et al.*, 1986; Kirchner *et al.*, 2000]. Figure 2.1 illustrates the lumped parameter model concept for determining the residence time of water draining a catchment. Environmental tracers are applied naturally during precipitation and are transported to the stream network along diverse surface and subsurface flow paths within the catchment. In most undisturbed catchments, however, flow paths are predominantly subsurface [Dunne and Leopold, 1978]. The residence time through the stream network is generally much shorter than transport through the catchment's subsurface and is thus ignored in catchment residence time distributions [see Kirchner *et al.*, 2001; Lindgren *et al.*, 2004]. The transport process along subsurface flow paths causes delay (due to advection) and spreading (dispersion) of tracer arrival in the stream network, which is a direct reflection of the catchment's flow path distribution, runoff processes, and subsurface hydrologic characteristics. The integrated response of tracer arrival at the catchment outlet from all locations in the catchment is described by the RTD.

Mathematically, this can be expressed by the convolution integral, which states that the stream outflow composition at any time,  $\delta_{out}(t)$ , consists of tracer,  $\delta_{in}(t-\tau)$ , that fell uniformly on the catchment in the past, which becomes lagged according to its residence time distribution,  $g(\tau)$ :

$$\delta_{out}(t) = \int_0^{\infty} g(\tau) \delta_{in}(t-\tau) d\tau = g(t) * \delta_{in}(t) \quad (5)$$

where  $\tau$  are the lag times between input and output tracer composition, and the asterisk represents the short-hand of the convolution operation. Equation 5 is similar to the linear systems approach used in catchment unit hydrograph models [e.g., Dooge, 1973], where

precipitation impulses are converted to an output response by linear superposition of a system response function (i.e.,  $g$ ). The unit hydrograph model predicts the response of an addition of potential energy (i.e., from effective precipitation) whereas Eqn. 5 predicts the tracer composition response in the stream to tracers applied during rainfall. Thus, the timescale of the runoff response (i.e., the dissipation of potential energy) is different than the residence time because fluctuations in hydraulic head can propagate much faster through the catchment than the transport of conservative tracer or individual water molecules [see *Torres, 2002*].

The lumped parameter approach (Eqn. 5) is valid only for steady-state conditions or when the mean subsurface flow pattern does not change significantly in time [*Zuber, 1986*]. It can be re-expressed with both  $t$  &  $\tau$  replaced by accumulated flow [*Nyström, 1985*] or corrected as flow-time [*Rodhe et al., 1996*]:

$$t_c = \int_{t_0}^t Q(t) dt / \bar{Q} \quad (6)$$

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. For example, 1 day would be equivalent to 1 mm of discharge volume if  $\bar{Q} = 365 \text{ mm y}^{-1}$ . During dry periods, time effectively becomes compressed, whereas during wet periods, time is expanded. Alternatively, mass flux (i.e.,  $C_{in}(t) \times I(t)$  and  $C_{out}(t) \times Q(t)$ , where  $C$  is concentration and  $I$  is input water flux) can be convolved instead of concentration [*Niemi, 1978; Zuber, 1986*]. Equation 5 without flow-corrected time and using only the concentration of tracer is suitable for catchments where flow parameters (e.g., velocity) do not deviate significantly from the long-term mean values or

where the variable portion of the flow system is small compared to the total subsurface volume. *Zuber et al.* [1986] found that when changes in the volume and flow rates are small compared to the mean residence time, variable flow systems do not deviate significantly from the steady-state case. A more general lumped model can be written as:

$$\delta_{out}(t) = \int_0^{\infty} g(t, \tau) \delta_{in}(\tau) d\tau \quad (7)$$

where the residence time distribution,  $g(t, \tau)$ , is permitted to be time varying, e.g., during non-steady conditions. Although Eqn. 7 is more realistic in a catchment context, the residence time distribution is inherently more complex and therefore difficult to quantify. *Turner et al.* [1987] treated the catchment residence time distribution stochastically, which enabled them to estimate the time-variable mean residence time of the stream. One might also consider the residence time to vary depending on antecedent wetness or some other description of the catchment state, since residence time, much like hydraulic conductivity, is expected to increase as the catchment becomes “hydrologically connected.”

### 2.3.1 Residence Time Distributions

RTDs used in Eqn. 5 are time-invariant, spatially-lumped characteristics of the catchment and thus describe the average catchment behavior of all factors that affect flow and tracer transport. The convolution approach implicitly assumes transport mechanisms, since parameters of the RTD are determined by solving the inverse problem based on tracer data (i.e., parameters for the RTD are estimated from known input/output tracer

records). A catchment's RTD could have various shapes depending on the exact nature of its flow path distribution and flow system assumptions. Thus, RTDs are assumed or selected from many possible distributions (as shown in Figure 2.1), since the true distribution is unknown and cannot be determined directly by experiment. Common model types (i.e., RTDs) used in hydrologic systems include: piston flow, exponential, exponential-piston flow, and dispersion models [*Maloszewski and Zuber, 1982; Cook and Böhlke, 2000*].

Figure 2.2 shows the form of these common RTDs. The piston-flow model, which is the most straightforward, implies that all flow pathways have the same velocities, which is never true in catchments. The exponential model, simply describes a catchment with flow pathways that are distributed exponentially, including pathways with very short residence times, except when formulated as the exponential-piston flow model. The dispersion model (from the one-dimensional solution of the advection-dispersion equation) can accommodate a range of RTDs with the addition of a second parameter,  $D/vx$  (inverse of the Peclet number), including formulations with short and dispersed (e.g., Figure 2.2, DM with  $D/vx = 0.6$ ) or near uniform (similar to the piston-flow model) (e.g., Figure 2.2, DM with  $D/vx = 0.01$ ) residence times. The example RTDs shown in Figure 2.2 illustrate that the choice and parameterization of different RTDs will affect the outflow tracer composition and interpretation of catchment response [*Turner and Barnes, 1998*]. Even though these models were developed for chemical engineering or groundwater applications, they have been used frequently with success in catchment systems [*Stewart and McDonnell, 1991; Vitvar and Balderer, 1997; DeWalle et al., 1997; Soulsby et al., 2000; McGuire et al., 2002; McGlynn et al., 2003*]. A detailed discussion

of models that have been used as RTDs is beyond the scope of this review; however, discussions of the main model types (Figure 2.2) can be found in *Maloszewski and Zuber* [1982; 1996] and *Turner and Barnes* [1998].

Recently, new models have been proposed such as the model of *Amin and Campana* [1996] that is capable of reproducing most of the aforementioned distributions (i.e., depending on the parameterization of their model). The *Amin and Campana* model has one or two additional fitting parameters compared to the distributions given by *Maloszewski and Zuber* [1982], but it is more flexible since it can represent many mixing possibilities (i.e., from no-mixing, to partial mixing, to perfect-mixing). *Maloszewski and Zuber* [1998] caution users of the lumped parameter approach by stating that even models with a low number of fitting parameters seldom yield unambiguous results. Additionally, they suggest that the terminology “mixing” is not adequate to describe subsurface flow systems, since significant mixing occurs only at the outlets of systems (e.g., streams, springs, and wells). *Kirchner et al.* [2001] developed a new model that is intended primarily for catchment systems. They derived an analytical expression for a spatially weighted advection-dispersion model for some common catchment geometries. They found that the shape of the spatially weighted advection-dispersion model approximated their previous empirical findings [see *Kirchner et al.*, 2000] by yielding fractal tracer behavior if the ratio of advective to dispersive timescales are similar (i.e., Peclet number  $\approx 1$ ) [see also, *Scher et al.* 2002].

The combination of residence time distributions and flow systems may also be used to approximate the integrated residence time of a multi-component flow system [*Maloszewski et al.*, 1983; *Uhlenbrook et al.*, 2002]. For example, in some catchments, a

two or three-component model is used to separate the rapid runoff components (e.g., Horton overland flow) from more delayed components (e.g., shallow subsurface flow or deep aquifers) to estimate catchment residence time based on the contribution from each component [Uhlenbrook *et al.*, 2002]. However, additional flow components should not be assumed on the basis of a poor fitting single component model, but according to a reasonable hydrological conceptual model that can be validated with other data (e.g., hydrometrics and geochemistry).

### 2.3.2 Modeling Methods

There are many modeling approaches to estimate residence times such as particle tracking [e.g., Molénat and Gascuel-Odoux, 2002], direct simulation [Goode, 1996], compartment models [Campana and Simpson, 1984; Yurtsever and Payne, 1986] and stochastic-mechanistic methods [Destouni and Graham, 1995; Simic and Destouni, 1999]. Often, these approaches require hydrological characterization of the catchment to develop models to approximate residence times. Many catchments lack data to benefit from these techniques, and thus, the lumped parameter approach is used to infer residence times from tracer data (natural or applied).

Lumped parameter methods provide estimates of catchment-scale hydrological parameters (i.e., residence time, transport velocities, storage) through an inverse procedure where the parameters are estimated by calibrating a RTD to fit simulations to measured tracer output composition [Maloszewski and Zuber, 1993; Oreskes *et al.*, 1994]. This is accomplished typically by numerically integrating the convolution integral (Eqn. 5) in the time domain. Several computer codes are available to perform this

procedure [*Maloszewski and Zuber, 1996; Bayari, 2002; Ozyurt and Bayari, 2003*]; nevertheless, it is easily implemented with practically any technical computing software. The fitting can be manual (i.e., trial and error) or automated using a variety of search algorithms that minimize one or several objective functions [e.g., *Legates and McCabe, 1999*]. Ultimately, other supporting hydrological evidence and intuition should be used to validate the selected model.

In the following two sections, we provide additional detail on methods that are absent or generally not well described in previous reviews of lumped parameter residence time modeling [e.g., *Maloszewski and Zuber, 1996; Turner and Barnes, 1998; Cook and Böhlke, 2000*], but are important approaches in catchment residence time modeling.

### 2.3.2.1 *The Frequency Domain*

While the convolution (Eqn. 2) is generally carried out in the time domain, it can be extended to the Fourier (i.e., frequency) or Laplace domain by using the respective transformations [*Dooge, 1973*]. Then, convolution is simply the product of the transforms of  $g(t)$  and  $\delta_{in}(t)$  according to the convolution theorem. A convolution can also be computed by the power spectra of  $g(t)$  and  $\delta_{in}(t)$ , which describes how much information is contained in a signal at a particular frequency determined by the square of the Fourier amplitudes [*Koopmans, 1995; Fleming et al., 2002*]. The power spectra are also convolved by multiplication. Lumped parameter models computed in the frequency domain have been described in detail by *Eriksson [1971]* and *Duffy and Gelhar [1985]* and subsequently used by *Kirchner et al. [2000]* to examine residence time distributions of catchments that have fractal stream chemistry (1/frequency). Not only is convolution



simplified in the frequency domain, but deconvolution is sometimes possible. Since convolution implies that the power spectra of the output series is equal to the product of the power spectra of the input series and residence time distribution:

$$o(t) = g(t) * i(t) \text{ and } |O(\omega)|^2 = |G(\omega)|^2 |I(\omega)|^2 \quad (8)$$

then the power spectrum of the residence time distribution is:

$$|G(\omega)|^2 = |O(\omega)|^2 / |I(\omega)|^2 \quad (9)$$

where  $\omega$  is frequency ( $\omega = 1/\lambda$ , where  $\lambda$  is wavelength),  $|I(\omega)|^2$ ,  $|O(\omega)|^2$ , and  $|G(\omega)|^2$  are the power spectra of the input, output, and residence time distribution, respectively.

$|G(\omega)|^2$  will give the degree of damping or attenuation of input frequencies according to its shape resembling a band-pass filter. While deconvolution (Eqn. 9) is possible, transformations of noisy data that involve fast Fourier transforms (if data are evenly spaced [see *Scargle*, 1982; *Kirchner et al.*, 2000]), can introduce erroneous high-frequency components that obscure the true residence time distribution when the transformation is numerically inversed [*Dietrich and Chapman*, 1993; *Viitanen*, 1997]. Recent approaches have been developed to constrain or stabilize deconvolution solutions [*Dietrich and Chapman*, 1993; *Skaggs and Kabala*, 1994; *Skaggs et al.*, 1998]; however, care must be taken when deconvolving noisy signals, since the problem is considered ill-posed.

### 2.3.2.2 The Sine-wave Approach

A common simplification used to estimate residence time using the lumped parameter model takes advantage of the strong seasonal changes in the composition of

stable isotopes in precipitation at temperate latitudes [Fritz, 1981; Stichler and Herrmann, 1983; Pearce *et al.*, 1986; Leopoldo *et al.*, 1992; Buzek *et al.*, 1995; DeWalle *et al.*, 1997; Burns and McDonnell, 1998; Burns *et al.*, 1998; Soulsby *et al.*, 1999]. The stable isotope composition of precipitation tends to reflect the seasonally varying tropospheric temperature variations (with relatively uniform precipitation) [see Dincer and Davis, 1984; Herrmann and Stichler, 1980], which can be approximated with a sine-wave function [Maloszewski *et al.*, 1983; DeWalle *et al.*, 1997]:

$$C_{in}(t) = A_n \sin(ct) \quad (10)$$

where  $A_n$  is the input amplitude,  $C_{in}$  is the input isotopic composition, and  $c$  is the angular frequency constant ( $2\pi/365$ ) in  $\text{rad d}^{-1}$  [Maloszewski *et al.*, 1983]. Likewise, a sine-wave output function with a damped amplitude and phase lag can be defined when Eqn. 10 is applied to the convolution integral:

$$C_{out}(t) = B_n \sin(ct + \phi) \quad (11)$$

where  $B_n$  is the output amplitude that is damped compared to  $A_n$ ,  $C_{out}$  is the output isotopic composition, and  $\phi$  is the phase lag or time of annual peak  $C_{out}$  in radians. The amplitudes of Eqns. 10 and 11 can be determined directly from observed input and output isotope records using a periodic regression model of the form [Bliss, 1970]:

$$\delta = \beta_0 + A[\cos(ct - \phi)] \quad (12)$$

where  $\delta$  is the predicted isotopic composition,  $\beta_0$  is the estimated mean annual  $\delta^{18}\text{O}$ ,  $A$  is the annual amplitude of  $\delta$ , and  $t$  is the time in days after an arbitrary date. Equation 12 can be evaluated statistically using sine and cosine terms (i.e., the first harmonic) as independent variables in a standard multiple regression model [Bliss, 1970]:

$$\delta = \beta_0 + \beta_{\cos} \cos(ct) + \beta_{\sin} \sin(ct) \quad (13)$$

The estimated regression coefficients,  $\beta_{\cos}$  and  $\beta_{\sin}$ , are used to compute  $A = \sqrt{\beta_{\cos}^2 + \beta_{\sin}^2}$

and  $\tan \phi = |\beta_{\sin}/\beta_{\cos}|$ .

Therefore, all terms in the model (Eqn. 5) are known except for the parameters of an assumed RTD. Analytical solutions for mean residence time parameter for the exponential (EM), exponential-piston flow (EPM), and dispersive (DM) models can be derived by combining Eqns. 5, 10, and 11:

$$\tau_m = c^{-1} \sqrt{f^{-2} - 1} \quad (\text{EM}) \quad (14)$$

$$\tau_m = \frac{\eta \sqrt{f^{-2} - 1}}{c} \quad (\text{EPM}) \quad (15)$$

$$\tau_m = c^{-1} \sqrt{-(\ln f) Pe} \quad (\text{DM}) \quad (16)$$

where  $f$  is the damping coefficient,  $B_n/A_n$ ;  $\eta$  is a parameter that describes the piston flow portion of the model; and  $Pe$  is the Peclet number. The parameter  $\eta$  is equal to the total volume of water in the system divided by the exponential volume. For  $\eta=1$ , the model is equivalent to the exponential model, whereas when  $\eta \rightarrow \infty$ , the model approaches pure piston flow [Maloszewski and Zuber, 1982]. The derivation of Eqns. 14 and 16 are given by Kubota [2000], since they were not included in the original work of Maloszewski *et al.* [1983]. Rather than assuming values for  $\eta$  (i.e., using Eqn. 15), Asano *et al.* [2002] calibrated Eqn. 11 with observed data by finding solutions for  $B_n$  and  $\phi$  using the exponential-piston flow model:

$$B_n = A_n \left( 1 + \frac{\omega^2 \tau_m^2}{\eta^2} \right)^{-1/2} \quad (17)$$

$$\phi = \omega\tau_m \left(1 - \frac{1}{\eta}\right) - \arccos \left[ \left(1 + \frac{\omega^2 \tau_m^2}{\eta^2}\right)^{-1/2} \right] \quad (18)$$

This approach allows for interpretation of the tracer signal using both the exponential and exponential-piston models.

Application of the sine-wave analysis is limited to conditions where Eqn. 12 (or 13) adequately fits the observed data. Therefore, regression statistics (e.g., coefficient of determination, root mean square error, etc.) should be provided to indicate potential uncertainty in the estimates of the mean residence time using Eqns. 14, 15, and 18. Flux-weighted (i.e., using recharge or precipitation, see below) inputs should be used in the sine-wave analysis in order to better characterize the tracer mass that contributes to outflow [e.g., see *Soulsby et al.*, 2000]. In a comparison of three different methods used to estimate mean residence times, *Stewart and McDonnell* [1991] found that the convolution approach provided better results than the sine-wave method. Likewise, sine-wave mean residence times computed from periodic regression data provided by *McGuire et al.* [2002], over-estimated their mean residence time results by an order of magnitude. This highlights the importance of weighting procedures in catchment studies where precipitation or recharge may not be uniform, which is generally assumed in application of the sine-wave method.

Since the sine-wave method is computationally simple, it is often used to estimate mean residence times. Nonetheless, it does not allow for the evaluation of different model types, since the mean residence time is computed directly from the signal amplitudes. Also, the sine-wave technique does not take advantage of more subtle variations at frequencies other than the annual frequency, which are common in stable

isotope data sets. Thus, either the power spectrum or convolution approach is preferred to more accurately estimate the RTD and evaluate the potential of different models. However, the sine-wave method can be used to approximate the maximum potential catchment mean residence time that the models are capable of estimating. For instance, *DeWalle et al.* [1997] calculated the maximum potential mean residence time of an exponential model using the minimum analytical reproducibility of isotope determinations as the output amplitude. The observed precipitation amplitude in their study was 3.41‰, which yielded a maximum stream water mean residence time of 5 years for a given  $\delta^{18}\text{O}$  error of 0.1‰. Therefore, depending upon the amplitude of the input (and of course the noise/signal relationship), one can approximate the maximum residence time possible based on the stable isotope data series.

#### ***2.4 Assumptions and Unresolved Issues of Catchment Residence Time Models***

Stream water residence times have been estimated for catchments at a variety of scales in diverse environments around the world [e.g., *Burgman et al.*, 1987; *Maloszewski et al.*, 1992; *Vitvar and Balderer*, 1997; *Frederickson and Criss*, 1999; *Kirchner et al.*, 2000; *Soulsby et al.*, 2000; *Asano et al.*, 2002; *Michel*, 2004; *McGuire et al.*, submitted]. Table 2.1 summarizes the findings from these and other studies that have evaluated the residence time of stream water using lumped parameter methods. Most studies have shown that mean residence times range from approximately <1 to 5 years and that assumed distributions vary depending upon various factors including hydrogeological attributes, suitability of fit to data, and data limitations. Often the assumptions and problems associated with the methods presented above are not clearly stated in the

literature. We argue that there are assumptions and unresolved issues that need to be synthesized in order to advance residence time estimation and modeling at the catchment scale. The application of lumped parameter tracer models to catchments is predicated on: 1) the input characterization issue, 2) the recharge assumption, 3) the data record length problem, 4) the stream sampling issue, 5) the residence time distribution selection problem, and 6) the model evaluation process. Each of these issues is discussed below by the evaluation and review of past residence time modeling approaches and through the use of new examples that illustrate outstanding problems for residence time estimation in catchments.

#### *2.4.1 The Input Characterization Issue*

Measured inputs are assumed to represent the spatial and temporal inputs for the entire catchment. In practice, the isotopic composition of precipitation is usually sampled at one location and as volume-weighted, bulk sample for weekly or monthly time intervals. At the catchment scale, elevation, rainfall intensity, air temperature, and rain shadow effects may cause considerable variation in the isotopic composition of precipitation over short distances, particularly in mountainous areas [Ingraham, 1998].

Figure 2.3 shows the  $^{18}\text{O}$  composition and rainfall amount over a 62 km<sup>2</sup> catchment in the western Cascades of Oregon, USA. There is a general persistence in the pattern of  $\delta^{18}\text{O}$  that is related the basin topography and storm track.  $\delta^{18}\text{O}$  tends to be more depleted in high elevation areas, specifically along the southern and eastern ridges of the basin. The elevation effect [Dansgaard, 1964] was  $-0.26\text{‰}$  per 100 m of elevation ( $r^2=0.45$ ) for these three consecutive storms, which is similar to results found by other

investigators [*Clark and Fritz, 1997*]. Rainfall amounts do not explain significantly more variance ( $r^2=0.49$ ) than elevation alone for the data in Figure 2.3; however, including a storm indicator variable in the regression model increases the  $r^2$  to 0.61, suggesting that storm track is also an important variable describing the  $\delta^{18}\text{O}$  patterns [see also *Pionke and DeWalle, 1992*]. Since the majority of catchment studies are located within upland (and sometimes mountainous) terrain, this example illustrates the need to properly characterize potential variations in space and time of inputs to a catchment. Figure 2.4 describes how considerable error can accrue in parameter estimates of catchment mean residence time if inputs are assumed to vary according to the elevation effect (Figure 2.3). The range of residence time model simulations shown in Figure 2.4 illustrates the effect of propagating a uniform distribution of  $\delta^{18}\text{O}$  random errors in precipitation through the residence time model. The amount of error is approximately equal to the expected range of  $\delta^{18}\text{O}$  applied to this catchment based on the elevation effects shown in Figure 2.3. Although this analysis neglects topographic persistence of the rainfall composition and many other processes (e.g., storm track), it illustrates that poor characterization of input tracer composition can lead to considerable uncertainty in residence time parameter estimates.

Snowmelt inputs can also be problematic, particularly in areas where it is the predominant form of soil water and groundwater recharge. Isotopically light snowmelt signatures can enhance the seasonality of the input and applicability of the sine-wave method for estimating residence time [e.g., *Maloszewski et al., 1983*]. Fractionation processes often cause the early snowmelt composition to be isotopically light and subsequent melt progresses toward heavier isotopic composition [*Unnikrishna et al.,*

2002]. Therefore, in the presence of snowcover, the input should be estimated from the snowmelt discharge (e.g., using snow lysimeters) and not from the snowcover or bulk precipitation [*Herrmann et al.*, 1981; *Stichler and Herrmann*, 1983; *Taylor et al.*, 2002].

Overall, there has been little research on how to obtain representative snowmelt composition in a catchment from spatial melt patterns for residence time estimates. Characterizing catchment isotopic input composition in general can be particularly challenging and poor characterization can potentially lead to significant uncertainty or error in the residence time modeling parameter estimates.

#### 2.4.2 *The Recharge Assumption*

Residence time models assume that the composition of inputs equals the composition of recharge that contributes to catchment turnover. The recharge timeseries, also called the input function [*Maloszewski and Zuber*, 1982], is not directly obtainable, even if the isotopic composition of precipitation is well known. Recharge represents the mass flux of water (i.e., volumetrically weighted isotopic composition) that infiltrates into the catchment and participates in runoff generation. Theoretically, if all precipitation inputs were measured and the recharge rates were known, then the weighted mean input determined from those two terms would balance the mean streamflow isotopic composition. This assumes no fractionation from either soil evaporation or canopy interception. Detailed discussion of fractionation processes that might affect recharge, can be found in *Gat and Tzur* [1967] and *DeWalle and Swistock* [1994]. Transpiration is not thought to fractionate water [*Wershaw et al.*, 1966; *Dawson and Ehleringer*, 1991].



Early methods approximated the recharge function by simply weighting the tracer composition by precipitation or by assuming that summer periods did not contribute to recharge [e.g., *Dinçer et al.*, 1970]. *Martinec et al.* [1974] developed a more sophisticated approach to estimate a monthly tritium recharge function in which a ratio of summer to winter precipitation was used as a fitting parameter in their model. *Grabczak et al.* [1984] found that the additional fitting parameter caused poor identifiability of the RTD parameters, and thus, developed an isotope mass balance approach to determine monthly infiltration coefficients. Assuming that groundwater is derived meteorically and that its isotopic composition is relatively constant in time, it can be calculated from the isotopic compositions ( $\delta$ ) of summer precipitation ( $P_s$ , where  $s$  = months 4, 5, 6, 7, 8, 9 or the months representing the growing season), and winter precipitation ( $P_w$ , where  $w$  = months 10, 11, 12, 1, 2, 3 or the months representing the non-growing season) [*Grabczak et al.*, 1984]:

$$\delta_G = (\alpha \sum \delta_s P_s + \sum \delta_w P_w) / (\alpha \sum P_s + \sum P_w) \quad (19)$$

where  $\delta_G$  is the isotopic composition of groundwater and  $\alpha$  is the infiltration coefficient equal to  $\alpha_s / \alpha_w$ , which is then:

$$\alpha = (\sum \delta_w P_w - \delta_G \sum P_w) / (\delta_G \sum P_s + \sum \delta_s P_s) \quad (20)$$

The infiltration coefficient ( $\alpha$ ) can be used to determine an input function ( $\delta_{in}$ ) for Eqn. 5 [*Bergmann et al.*, 1986; *Maloszewski et al.*, 1992]:

$$\delta_{in}(t) = \frac{N \alpha_i P_i}{\sum_{i=1}^N \alpha_i P_i} (\delta_i - \delta_G) + \delta_G \quad (21)$$

where  $\alpha_i$  are the individual infiltration coefficients corresponding the  $i$ th month, and  $N$  is the number of time periods (e.g., months) for which precipitation was collected.

*Maloszewski and Zuber* [1992] claim that  $\alpha$  computed from Eqn. 20 more realistically represents tracer mass compared to  $\alpha$  computed from hydrological data (i.e.,  $\alpha = (Q_s P_w)/(Q_w P_s)$ ), since it likely includes elevation effects and delayed isotopic input from snowpack storage.

A more flexible approach, which was introduced by *Martinez et al.* [1974] and later adopted by *Stewart and McDonnell* [1991] and *Weiler et al.* [2003], directly incorporates the recharge weighting,  $w(t)$ , into a modified convolution equation so that the streamflow composition reflects the mass flux leaving the catchment:

$$\delta_{out}(t) = \frac{\int_0^{\infty} g(\tau) w(t-\tau) \delta_{in}(t-\tau) d\tau}{\int_0^{\infty} g(\tau) w(t-\tau) d\tau} \quad (22)$$

The weighting term,  $w(t)$ , can include any appropriate factor such as rainfall rates, throughfall rates, or partially-weighted rainfall rates (e.g., effective rainfall). Also, Eqn. 22 can be combined with simple rainfall-runoff models based on unit hydrograph or transfer function approaches [*Jakeman and Hornberger*, 1993; *Young and Beven*, 1994] that allow for the identification of effective precipitation from a nonlinear soil moisture routine. In other words, a coupled hydrologic-tracer model can be constructed to describe the tracer and runoff behavior, in addition to identifying RTD parameters [cf. *Weiler et al.*, 2003]. Generally, transfer function models contain a minimal number of parameters that are often dictated by the information content in the data, and thus, are

considered to be among the most parsimonious models for simulating runoff [Young, 2003].

Soil water routines in conceptual hydrological models have recently been used to weight the isotopic composition of precipitation to represent recharge [Vitvar *et al.*, 1999; Uhlenbrook *et al.*, 2002]. Vitvar *et al.* [1999] compared weighting methods based on lysimeter outflow [cf. Vitvar and Balderer, 1997] and groundwater recharge calculated from the model PREVAH-ETH [Gurtz *et al.*, 1999] and found that modeled groundwater recharge gave the best fit to the observed isotopic data (Figure 2.5). They suggested that modeled recharge more accurately reflected the portion of precipitation that reached the aquifer, whereas the lysimeter outflow accounted for only shallow vertical flow processes. Figure 2.5 shows clearly that the input weighting based on the modeled groundwater recharge fits the observed baseflow  $\delta^{18}\text{O}$  compared to the lysimeter outflow weighting. While soil water balance models may provide better fits to data, they require additional parameters to describe soil properties and evapotranspiration, and thus, introduce potential uncertainty from the increased overall model complexity.

#### 2.4.3 The Data Record Length Problem

A common problem with the lumped parameter approach is the length of tracer record, in terms of both inputs and outputs. A short input can lead to poorly estimated parameters and tracer mass imbalance if the timescale of the RTD is sufficiently longer than the input record. This problem is most frequently encountered when stable isotopes are used as tracers, since tritium composition in precipitation is relatively well known [e.g., Michel, 1989]. Many investigators have extended stable isotope inputs using

temperature records [Burns and McDonnell, 1998; Uhlenbrook *et al.*, 2002], sine-wave approximations [McGuire *et al.*, 2002], and with data from nearby long-term stations [Maloszewski *et al.*, 1992; Vitvar and Balderer, 1997]. In such cases, uncertainty is introduced into the estimation of the RTD parameters; thus, it is recommended to obtain the longest possible measured record. As a thought exercise, consider Figure 2.6 where a measured input record length is equal to the catchment mean residence time ( $\tau_m$ ) for an exponential RTD. The mass recovery for that system is 63% (i.e.,  $1 - e^{-1}$ ) of the time equivalent to the length of the input record, which is the amount of input water leaving the system with an age less than or equal to  $\tau_m$  (Figure 2.6). In other words, a 1-year mean residence time requires about 5 years of input record to pass 100% of those inputs through the basin. If the mean residence time was 25% of the input record length (e.g., 3 months), then approximately 100% of the inputs could pass through the catchment in a period of time equal to the time in which inputs were collected (e.g., 1 year) (Figure 2.6).

The convolution is essentially a frequency filter [cf. Duffy and Gelhar, 1985] which means that more repetitive frequencies at all wavelengths will allow for better identification of the RTD. Thus, if one is interested in long timescales of the catchment RTD (i.e., annual to multi-year), then several of those cycles should be “sampled” by the input time series. In practice, we deal typically with records on the order of several years; however, Kirchner *et al.* [2000] demonstrate that long-term (and high frequency) measurements allow for the evaluation of catchment RTDs that span several orders frequency magnitude (i.e., from timescales of days to multi-year). In some cases, a short timeseries can be used if there are pronounced tracer variations in both the input and output data over the timescales of interest. For example, Stewart and McDonnell [1991]

were able to model soil water  $^2\text{H}$  fluctuations using a 14-week dataset because the observed isotopic composition had a consistent, strong variation with an approximate 5-week period and expected mean residence times that were on the order 2 to 20 weeks.

In a re-interpretation of a tritium record, *Zuber et al.* [1992] extended previously published data record [cf. *Grabczak et al.*, 1984] with new tritium observations and found, as in the original work, similar RTD parameters for a two-component dispersion model. However, better results were achieved by selecting single component models using the updated observations, which reduced the number of fitting parameters and yielded a more reliable model [*Maloszewski and Zuber*, 1993]. In a similar effort, *Vitvar et al.* [1999] reanalyzed  $^{18}\text{O}$  data from several sites presented in *Vitvar and Balderer* [1997] that were extended an additional year and found relatively similar parameters for the RTDs. *Uhlenbrook and Scissek* [2003] also found that results from a reanalysis produced similar residence time estimates for the Brugga catchment in Germany as in the original study [*Uhlenbrook et al.*, 2002]. Even though they were able to confirm previous results, the longer observation record (i.e., 2 additional years) did not reduce the uncertainty interval of the parameter estimates ( $\pm 0.5$  y). Considering the limited number of examples in the literature, it is difficult to recommend the record length needed to reliably estimate RTDs. In most published studies (Table 2.1), outflow records lengths are approximately 2 to 4 years, while input records are typically longer (e.g., 2 to 10 years), often containing estimated or extrapolated values for inputs prior to the time of outflow observations. In general, longer input and output data records produce more reliable estimates of the residence time distribution.

#### 2.4.4 *The Stream Sampling Issue*

Residence time models assume that inputs and outputs are sampled at the same temporal resolution. In most studies, the inputs are sampled as bulk weekly (or monthly) measurements; thus, the models cannot be expected to resolve stream composition for timescales finer than weekly (or monthly). Typically during sample collection, storm periods are excluded so that inputs that immediately affect the stream tracer composition are removed from the analysis [e.g., *Vitvar and Balderer, 1997; DeWalle et al., 1997; McGuire et al., 2002*]. This practice essentially aliases the timeseries, since the “true” signal contains higher frequencies, and creates bias toward older water in the residence time estimates. The stream sampling protocol will thus determine what residence time is estimated in the study, e.g., reflecting baseflow or the entire flow regime.

Alternatively, *Maloszewski et al. [1983]* and *Buzek et al. [1995]* used a simple two-component mixing model to separate the direct influence of the rapid runoff component from the slower subsurface component for which they were interested in determining the RTD. In a new hydrograph separation approach, *Weiler et al. [2003]* show examples of event-water residence time distributions (i.e., the rapid component) that persist for 15 to 20 hours after the storm event in an extremely responsive basin. Therefore, conservatively, a lag time of one or two days after the storm may be necessary to avoid the rapid contribution of event water. If inputs are sampled at finer time intervals (e.g., daily), then this issue becomes moot and the timescales that can be resolved for the catchment residence time decrease. *Kirchner et al. [2000; 2001; 2004]* have demonstrated based on spectral analysis that high temporal resolution observations

can lead to new insights into the structure and function of catchments. Essentially, the stream tracer timeseries must match the temporal resolution of the input record and the RTD timescale of interest.

#### 2.4.5 *The RTD Selection Problem*

A common issue in residence time modeling is selecting an appropriate residence time distribution (RTD) that describes the actual flow conditions of the catchment. The lumped parameter approach has been applied predominantly to groundwater systems and as such, many of the aforementioned RTDs (Figure 2.2) have been used to represent groundwater flow conditions. Consequently, the selection of model types is often based on simplified assumptions regarding aquifer geometries [e.g., see *Cook and Böhlke*, 2000; *Maloszewski and Zuber*, 1982] and not specific catchment attributes. For instance, an exponential RTD, by far the most popular RTD used to date (see Table 2.1), would result from an unconfined aquifer with uniform hydraulic conductivity and thickness [*Maloszewski and Zuber*, 1982]. *Eriksson* [1958] has suggested that the exponential model could also approximate the case of decreasing hydraulic conductivity with depth in an aquifer. This hydraulic conductivity decrease with depth is a defining feature of catchment hydrologic response [*Beven*, 1982] and fundamental to our catchment models in use today [*Ambroise et al.*, 1996]. In another example, a partially confined aquifer could be considered to delay or effectively eliminate contribution from short residence times, thus producing a RTD such as the exponential-piston flow model. In general, the RTD simply describes the integrated effect of all flow pathways expressed at the discharge location of a flow system or in the case of catchments, at the basin outlet. The

assumption that we can match a RTD with functional catchment behavior is one of the biggest challenges in the application of residence time models in catchment hydrology.

There has been little theoretical work on determining the form of the RTD for catchments. One might expect a catchment RTD to conform to examples from groundwater flow systems. In a theoretical analysis on subsurface flow systems in catchments, *Haitjema* [1995] demonstrated that the RTD of any basin shape, size, and hydraulic conductivity is exponential given that the flow system is steady, not stratified, and receives uniform recharge. *Haitjema* [1995] also proposed that the exponential RTD could successfully approximate RTDs for some non-steady cases. Some experimental results support *Haitjema's* [1995] findings of exponential RTDs for catchments; such as the covered catchment study at Gårdsjön by *Rodhe et al.* [1996]. In a later study, *Simic and Destouni* [1999] derived the RTD produced in *Rodhe et al.* [1996] with little calibration. They used a stochastic-mechanistic model that described nonuniform flow velocity resulting from groundwater recharge through the unsaturated zone. The model also incorporated preferential flow, diffusional mass transfer between mobile and relatively immobile water, and random heterogeneity resulting from spatially variable transmissivity.

In other experimental work, spectral analysis of daily chloride concentrations in rainfall and runoff at several sites around the world contest the use of exponential RTDs as the standard RTD in catchments. *Kirchner et al.* [2000] found that conventional catchment transport models (e.g., exponential and dispersive) could not reproduce the spectral characteristics (i.e., fractal or  $1/\omega$  scaling) that were observed in stream chloride concentrations. They suggested instead that a gamma function, parameterized with a



shape parameter of about 0.5, was the most appropriate RTD for the catchments in their study. *Kirchner et al.* [2001] demonstrate that advection and dispersion of spatially distributed rainfall inputs can produce the same fractal scaling behavior observed in *Kirchner et al.* [2000] when the dispersivity length scale approaches the length of the hillslope (i.e., Peclet  $\approx 1$ ). Even though such low Peclet numbers seem unrealistic (i.e., the dispersivity length approaches the length of the flow field [see *Gelhar et al.*, 1992]), *Kirchner et al.* [2001] claim that it accounts for the large conductivity contrasts in hillslopes. In using the same model as *Simic and Destouni* [1999], *Lindgren et al.* [2004] also found that the ratio of advective to dispersive transport timescales are nearly equivalent. Even when the ratio was increased by one order of magnitude, they were still able to reproduce a fractal tracer behavior as observed by *Kirchner et al.* [2000].

Notwithstanding, the potential effects of hillslope topography and catchment geometry were not specifically addressed by *Lindgren et al.* [2004] and have recently been shown to control catchment-scale mean residence time [see *McGuire et al.*, submitted]. Both *Lindgren et al.* [2004] and *Kirchner et al.* [2001] used artificial catchment spatial representations (i.e., rectangular and other simple geometries); however, the complexity of the topography likely influences catchment-scale transport. For example, Figure 2.7 shows two different RTDs calibrated from  $^{18}\text{O}$  input/output data collected from six catchments in the western Cascades of Oregon [cf. *McGuire et al.*, submitted]. The exponential RTDs closely approximate a RTD computed from an advection-dispersion model weighted by the catchment flow path distribution determined from a DEM (digital elevation model) analysis. Thus, in a similar approach to *Kirchner et al.* [2001], transport from spatially distributed inputs occurs through simple advection

and dispersion processes, but in this case, along pathways represented by the true catchment geometry and topography. The spatially weighted advection-dispersion RTDs for several of the catchments contain the short-term responsive and long-term broad tailing behavior observed in *Kirchner et al.* [2000], but do not exhibit  $1/\omega$  scaling. Using the DEM to represent the potential flow path variation allows for catchment-specific features such as long hillslopes (e.g., WS08 in Figure 2.7) and highly varied topography to be incorporated into the shape of the RTD, yielding potentially more realistic distributions. Additionally, this spatial advection-dispersion model and that which is presented in *Kirchner et al.* [2001] contain only two parameters (i.e., the Péclet number and mean residence time of the dispersion model). Incidentally, Péclet numbers used to calibrate the spatial advection-dispersion model that represent average transport behavior at the catchment-scale in Figure 2.7, range from 9 to 500 with a median of 29; thus, they seem to fall within the range of values reported from field studies, including the frequently observed increase with scale (i.e., basin area) [see *Gelhar et al.*, 1992].

Identifying plausible RTDs for use in catchments will require both experimental and theoretical developments for a more comprehensive understanding of transport at the catchment-scale. For example, *Lindgren et al.* [2004] were able to show from a theoretical process perspective that the results of *Kirchner et al.* [2000] are explainable by considering variable groundwater advection, including preferential flow, and mass transfer between mobile and immobile zone in the subsurface system. In general, there appears to be no consensus on a functional representation of the RTD for catchments. However, with continued development of new techniques that describe first-order process controls on residence time (e.g., immobile/mobile zones, soil depth, hydraulic

conductivity), long-term datasets sampled at high frequency, and approaches that utilize information contained within DEMs such as catchment geometry and topography, we will gain new insights into the RTD representation at the catchment-scale.

#### 2.4.6 *The Model Evaluation Process*

In current practice, RTDs are selected based either on an assumed flow system as we described for aquifers or by the best fitting results from various model simulations (i.e., through calibration). Selecting a model through calibration, which is usually based on objective measures such as the sum of squared residuals or Nash-Sutcliffe efficiency [Nash and Sutcliffe, 1970], can be problematic since parameters are often not identifiable and different models types can equally fit observations [Beven and Freer, 2001]. The evaluation of parameter sensitivity and uncertainty has not been included customarily in the application of residence time models, even though it has received significant attention in the rainfall-runoff modeling [Bergström, 1991; Seibert, 1997; Uhlenbrook *et al.*, 1999; Beven, 2001] and tracer-based hydrograph separation model [Bazemore *et al.*, 1994; Genereux, 1998; Joerin *et al.*, 2002] literature. Since the lumped parameter approach is focused on parameter estimation, we do ourselves disservice by not addressing quantitatively the reliability of our results. In some cases, more than one model may equally describe the system [Vitvar and Balderer, 1997; McGuire *et al.*, 2002]. Thus, it can be argued that the given errors in our measured signals and the complexity of catchments, that there will be many acceptable representations of the system [Beven and Freer, 2001].

Therefore, when evaluating possible RTDs through calibration it is recommended to also evaluate parameter identifiability and sensitivity. Figure 2.8 demonstrates schematically the model evaluation process. In this example, two seemingly similar residence time model results are compared: the gamma model [see *Kirchner et al.*, 2001] and the exponential model. The simulations of the two RTDs models have approximately the same goodness-of-fit to observations (Nash-Sutcliffe  $E = 0.53$  for the gamma model, and  $E = 0.48$  for the exponential model); however, the scale parameter for the gamma model ( $\beta$ ) cannot be estimated with any confidence as noted by the absent minima in the scattergram of Monte Carlo results shown in the parameter identifiability box in Figure 2.8. The sensitivity plot for the gamma model shows that the scale parameter does not deviate significantly from zero, indicating that it is insensitive across the entire time series. Alternatively, the exponential model, which only has one parameter, becomes sensitive mainly during the winter periods of 2001 and 2002. A temporal sensitivity analysis may be used to evaluate parameter cross correlation or suggest critical time periods for optimizing parameter estimation in future studies. For example, in Figure 2.8, summer  $^{18}\text{O}$  composition does not appear to significantly influence the parameter estimates, which might suggest that sample collection should focus on late fall and winter periods. The principle reason for a temporal sensitivity analysis, however, is to evaluate model performance and discriminate between potential RTDs. Several techniques that are available include dynamic identifiability analysis [*Wagner et al.*, 2003] and the use of the parameter covariance matrices [*Knopman and Voss*, 1987]. Many of these techniques also allow for the computation of confidence limits on parameter estimates and simulations; however, consideration of input

uncertainty should be included for a comprehensive uncertainty analysis of catchment residence time distributions. Model testing and evaluation should be included in any modeling exercise.

## ***2.5 Summary and Outlook***

We have attempted to evaluate and review the residence time literature in the context of catchments and stream water residence time estimation. Our motivation for this work relates to the new and emerging interest in residence time estimation in catchment hydrology and the need to distinguish between approaches and assumptions originating in the groundwater literature from catchment applications. Our intent has been to provide a formal clarification on the assumptions, limitations, and methodologies in applying residence time models to catchments, while highlighting new developments in research. Our review has focused on lumped parameter approaches of estimating residence times for streams and catchments, since it provides a quantitative approach to fundamentally describing the catchment flow system. The approach relies primarily on tracer data, and thus, is useful in gauged and ungauged basins and as a complement to other types of hydrological investigations. We have provided a critical analysis of unresolved issues that should be evaluated in future research through the application of lumped parameter residence time modeling at the catchment scale. These issues included: 1) the input characterization issue, 2) the recharge assumption, 3) the data record length problem, 4) the stream sampling issue, 5) the residence time distribution selection problem, and 6) the model evaluation process. Despite the fact that many of the approaches discussed in this review are in their infancy (e.g., the spectral analysis of

tracer data and theoretical, mechanistic and spatially derived models of residence time distributions), it is clear that residence time modeling will provide significant advances in catchment hydrology and improvement in understanding physical runoff generation processes and solute transport through catchments.

## 2.6 References

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Table 2.1. Summary of published field studies in which residence time was estimated for streamwater<sup>†</sup>.

Reference & Site	Basin Area [km <sup>2</sup> ]	Tracer	Time Series Length		Models <sup>a</sup>		Parameters <sup>b</sup>		
			Input [y]	Output [y]	Method	Type	$\tau_m$ [y]	$D_p$ [-]	$\eta$ [y]
<i>Asano et al.</i> [2002], Fudoji	0.001	<sup>2</sup> H	1	1	SW	EM	>1		
Rachdani	0.002	<sup>2</sup> H	1	1	SW	EM EPM	1 1.1		1.37
<i>Begemann and Libby</i> [1957], Upper Mississippi (Rock Island)	n.a.	<sup>3</sup> H	n.a.	n.a.	WB	EM	15		
<i>Behrens et al.</i> [1979], Rofenache	96.2	<sup>3</sup> H	8	7.5	C	EM	4		
<i>Bergmann et al.</i> [1986], Pöllau	58.3	<sup>18</sup> O	4	4			1.9		
<i>Burgman et al.</i> [1987], Torn Älv	6000	<sup>18</sup> O	10	10	SW	EM	1.1		
Rickleån	1800	<sup>18</sup> O	10	10	SW	EM	2		
Öre Älv	2880	<sup>18</sup> O	10	10	SW	EM	1		
Ammerån	2500	<sup>18</sup> O	10	10	SW	EM	1		
Norrstöm	22600	<sup>18</sup> O	10	10	SW	EM	2.25		
Botorpsstr	1000	<sup>18</sup> O	10	10	SW	EM	0.67		
Ljungbyån	800	<sup>18</sup> O	10	10	SW	EM	0.33		
Lyckebyån	1100	<sup>18</sup> O	10	10	SW	EM	0.17		
Mörrumsån	3400	<sup>18</sup> O	10	10	SW	EM	0.6		
Tolångaån	440	<sup>18</sup> O	10	10	SW	EM	0.83		
Nissan	2800	<sup>18</sup> O	10	10	SW	EM	0.6		
<i>Burns and McDonnell</i> [1998], Woods Lake WO2	0.413	<sup>18</sup> O	1.5	1.3	SW	EM	0.28		
Woods Lake WO4	0.612	<sup>18</sup> O	1.5	1.3	SW	EM	0.28		
<i>Burns et al.</i> [1998], Winnisook	2	<sup>18</sup> O	1	1	SW	EM	0.90		
Winnisook	2	<sup>35</sup> S	n.a.	n.a.	MM	n.a.	0.68-0.87		
Shelter Creek	1.6	<sup>18</sup> O	1	1	SW	EM	1.03		
Shelter Creek	1.6	<sup>35</sup> S	n.a.	n.a.	MM	n.a.	0.51-0.83		
<i>Buzek et al.</i> [1995]									
<i>Cui</i> [1997], Rippach	1.2	<sup>18</sup> O	1	1	C	EPM	2.33		1.2
Rippach	1.2	<sup>18</sup> O	1	1	C	DM	1.6	0.25	
Loechembach	1.7	<sup>18</sup> O	1	1	C	EPM	2.29		1.35
Loechembach	1.7	<sup>18</sup> O	1	1	C	DM	1.46	0.09	
<i>DeWalle et al.</i> [1997], Benner Run	11.34	<sup>18</sup> O	1	1	SW	EM	>5		
Fernow WS3	0.34	<sup>18</sup> O	1	1	SW	EM	1.6		
Fernow WS4	0.39	<sup>18</sup> O	1	1	SW	EM	1.4		
<i>Dinçer et al.</i> [1970], Modry Dul	2.65	<sup>3</sup> H	8	2.5	C, $\alpha=0$	BM	2.5		
<i>Eden et al.</i> [1982], Kreidenbach	1.85	<sup>18</sup> O	2	2	SW, m1 SW, m2	EM EM	0.7 1.4		
<i>Eriksson</i> [1958], Upper Mississippi, (Rock Island)	n.a.	<sup>3</sup> H	n.a.	n.a.	WB	EM	8		



Table 2.1 continued.

Reference & Site	Basin Area [km <sup>2</sup> ]	Tracer	Time Series Length		Models		Parameters		
			Input [y]	Output [y]	Method	Type	$\tau_m$ [y]	$D_p$ [-]	$\eta$ [y]
<i>Frederickson and Criss</i> [1999], Meramec River	10, 300	<sup>18</sup> O	3	3	ExpAve	--	0.3		
<i>Herrmann et al.</i> [1999], VAHMPIRE <sup>c</sup>	n.a.	<sup>3</sup> H	24	n.a.	C	EM DM	7-15 8-13	0.15	
<i>Holko</i> [1995], Jalovecky Creek	23	<sup>2</sup> H	3	2.5	C	DM	1.3	2.2	
<i>Kirchner et al.</i> [2001], Hafren Tanllwyth	3.47 0.51	Cl <sup>-</sup> Cl <sup>-</sup>	14 14	14 14	PS PS	Gamma Gamma	0.82 0.36		
<i>Leopoldo et al.</i> [1991], Búfalos Paraiso	1.58 3.27	<sup>18</sup> O <sup>18</sup> O	4 4	4 4	SW SW	EM EM	0.34 0.62		
<i>Maloszewski and Zuber</i> [1982], Modry Dul	2.65 2.65	<sup>3</sup> H <sup>3</sup> H	10 10	4 4	C, $\alpha=1$ C, $\alpha=0$	DM DM	5.5 3.6	1.6 0.25	
<i>Maloszewski et al.</i> [1983], Lainbach	18.7	<sup>2</sup> H <sup>2</sup> H <sup>3</sup> H <sup>3</sup> H <sup>3</sup> H <sup>3</sup> H	3 3 9 9 9 9	3 3 7 7 7 7	SW, m1 SW, m2 C, m1 C, m1 C, m2 C, m2	EM EM EM DM EM DM	1.1 2.1 1.8 1.6 2.2 2.4	0.15 0.15	
<i>Maloszewski et al.</i> [1992], Wimbactal	33.4 33.4 33.4	<sup>3</sup> H <sup>3</sup> H <sup>18</sup> O	40 40 9	3 3 3	C C C	EM DM EM	4.3 4.2 4.5	0.60	
<i>Martinec et al.</i> [1974], Dischma		<sup>3</sup> H			C	EM DM	4.0 4.8		
<i>Matsutani et al.</i> [1993], Kawakami	0.14	<sup>3</sup> H	6	4	MM/C	BN	2.5		
<i>McGlynn et al.</i> [2003], M15	0.026	<sup>3</sup> H	60	n.a.	C	PF EPM DM	1.1 1.5 1.3		n.a.
K	0.17	<sup>3</sup> H	60	n.a.	C	PF EPM DM	2.4 2.4 2.1		n.a.
PL14	0.8	<sup>3</sup> H	60	n.a.	C	PF EPM DM	2 2 1.7		n.a.
Bedload	2.8	<sup>3</sup> H	60	n.a.	C	PF EPM DM	2 2 1.7		n.a.

Table 2.1 continued.

Reference & Site	Basin Area [km <sup>2</sup> ]	Tracer	Time Series Length		Models		Parameters		
			Input [y]	Output [y]	Method	Type	$\tau_m$ [y]	$D_p$ [-]	$\eta$ [y]
<i>McGuire et al.</i> [2002], Brown	0.14	<sup>18</sup> O	3	1.3	C	EPM	0.8		1.28
LR1	1.23	<sup>18</sup> O	3	1.3	C	EPM	0.4		1.1
<i>McGuire et al.</i> [submitted], WS02	0.601	<sup>18</sup> O	3	2.3	C	EM	2.2		
WS03	1.011	<sup>18</sup> O	3	2.3	C	EM	1.3		
WS08	0.214	<sup>18</sup> O	3	2.3	C	EM	3.3		
WS09	0.085	<sup>18</sup> O	3	2.3	C	EM	0.8		
WS10	0.102	<sup>18</sup> O	3	2	C	EM	1.2		
MACK	5.81	<sup>18</sup> O	3	2.3	C	EM	2		
LOOK	62.42	<sup>18</sup> O	3	1.5	C	EM	2		
<i>Michel</i> [1992], Colorado above Cisco, UT	75000	<sup>3</sup> H	30	22	MM	EM	14.3		
Kissimmee above L. Okeechobee	4500	<sup>3</sup> H	30		MM	EM	2.5		
Mississippi at Anoka, MN	53000	<sup>3</sup> H	30	22	MM	EM	10		
Neuse at Vanceboro, NC	11000	<sup>3</sup> H	30		MM	EM	11.1		
Potomac at Rocks MD	27000	<sup>3</sup> H	30	22	MM	EM	20		
Sacramento at Sacramento	67000	<sup>3</sup> H	30	7	MM	EM	10		
Susquehanna above Harrisburg	70000	<sup>3</sup> H	30	19	MM	EM	10		
<i>Michel</i> [2004], Ohio River	215400	<sup>3</sup> H	33	23	MM	n.a.	10		
Missouri River	1073300	<sup>3</sup> H	44	34	MM	n.a.	4		
<i>Pearce et al.</i> [1986], M8	0.038	<sup>18</sup> O	3	3	SW	EM	0.33		
Rodgers [in press], Feshie Bridge	230.7	<sup>18</sup> O	1	1	SW	EM	0.3-0.55		
Allt Chomraig	44.9	<sup>18</sup> O	1	1	SW	EM	0.5-0.84		
Feshie Lodge	114.6	<sup>18</sup> O	1	1	SW	EM	0.18-0.37		
Upstream Braids	88.1	<sup>18</sup> O	1	1	SW	EM	0.13-0.30		
Eidart	29.9	<sup>18</sup> O	1	1	SW	EM	0.13-0.31		
Upper Feshie	32.3	<sup>18</sup> O	1	1	SW	EM	0.1-0.26		
Allt a' Mharcaidh	10	<sup>18</sup> O	1	1	SW	EM	0.72-1.22		
<i>Rodhe et al.</i> [1996], Gårdsjön	6300m <sup>2</sup>	<sup>18</sup> O	4	4	C <sup>d</sup>	EM <sup>d</sup>	0.18 <sup>d</sup>		
<i>Soulsby et al.</i> [2000],									
Allt a' Mharcaidh, G1	10	<sup>18</sup> O	3	3	SW	EM	>5		
Allt a' Mharcaidh, G2	1.69	<sup>18</sup> O	3	3	SW	EM	3.6		
Allt a' Mharcaidh, G3	2.96	<sup>18</sup> O	3	3	SW	EM	>5		
<i>Vitvar and Balderer</i> [1997], Rietholzbach	3.18	<sup>18</sup> O	18	2	C	DM	1.04	0.7	
Rietholzbach	3.18	<sup>18</sup> O	18	2	C	EPM	1.04		1.05
Oberer Rietholzbach	0.9	<sup>18</sup> O	18	2	C	EM	2		
<i>Vitvar et al.</i> [2002], Winnisook	2	<sup>18</sup> O	6	3	C	EPM	0.74		1.2
						DM	0.74	0.4	
<i>Zuber et al.</i> [1986], Lange Bramke	0.76	<sup>3</sup> H	5	5	C	EM	2.2		

<sup>†</sup>Information summarized/inferred from original reference and streamwater was typically taken as baseflow. For details on specific studies, see original reference. n.a. is not applicable or available.

<sup>‡</sup>Methods: C is convolution (m1 = model 1, m2 = model 2, usually related to direct v.s indirect streamflow [see reference];  $\alpha$  = recharge weighting factors [see reference]), SW is sine-wave, WB is water balance, MM is mixing model, PS is power spectra, ExpAve is exponential averaging model. Model: EM is exponential, EPM is exponential piston flow, DM is dispersion, PF is piston flow, Gamma is the gamma distribution and BN is the binominal distribution. n.a. is not applicable or available.

<sup>b</sup>  $\tau_m$  is mean residence time,  $D_p$  is the dispersion parameter (1/Peclet), and  $\eta$  is the piston flow parameter.

<sup>c</sup>Validating hydrological models using process studies Internal data from research basins, Vallcebre study basins, Pyrenees.

<sup>d</sup>Residence time distribution and modeling given in flow-time.

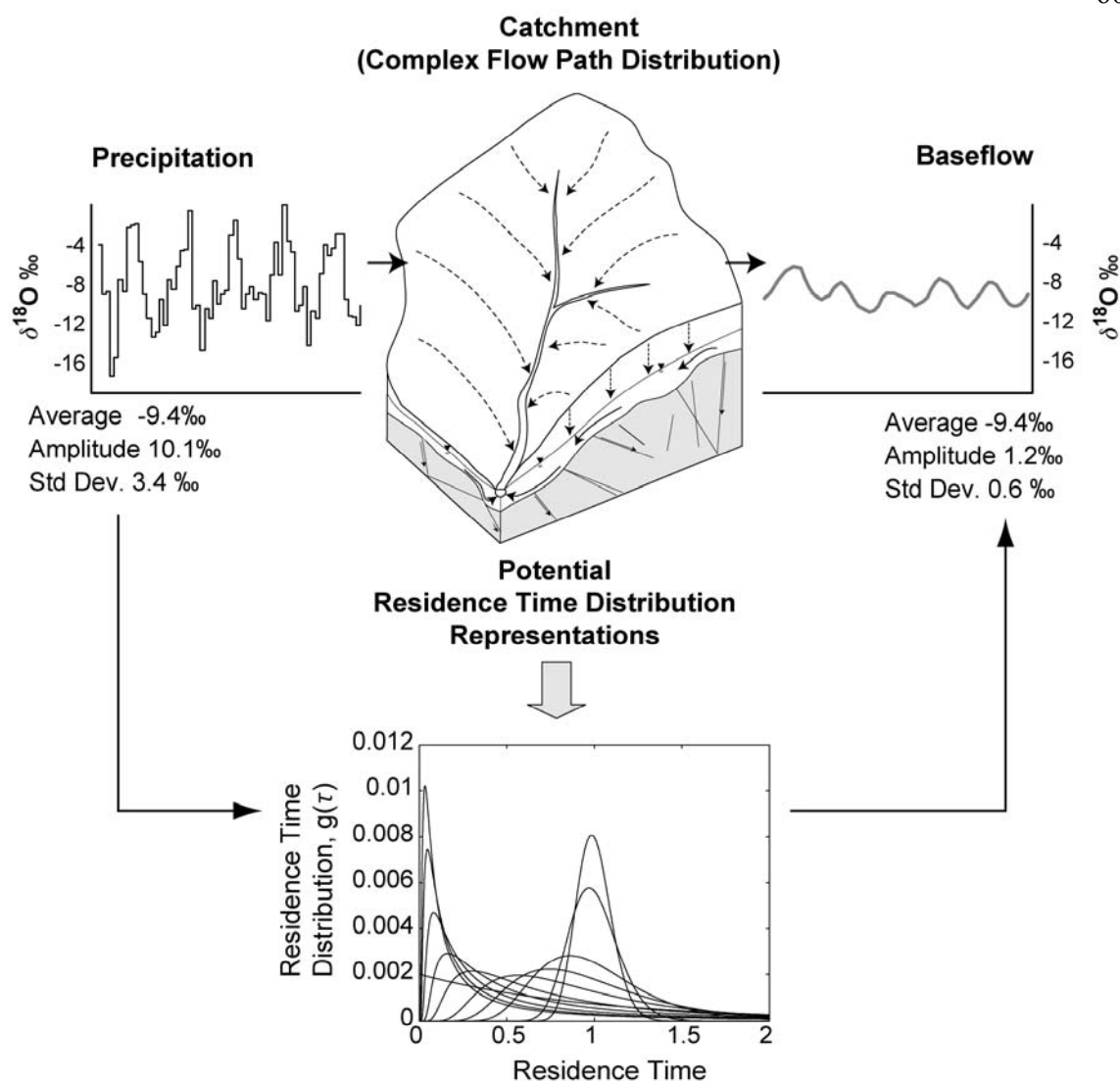


Figure 2.1. Conceptual diagram of the lumped parameter residence time modeling approach. Catchments receive temporal tracer (e.g.,  $\delta^{18}\text{O}$ ) inputs that are transported along diverse flow paths in the unsaturated and saturated zones as tracers migrate through the subsurface toward the stream network. The result of differential transport within the catchment is a tracer output signal (baseflow) that is damped (i.e., decrease in standard deviation and amplitude) and lagged compared to the input signal. The complex distribution of catchment flow paths is represented by a distribution of residence times,  $g(\tau)$ , that describe the integrated behavior of tracer transport through the catchment.

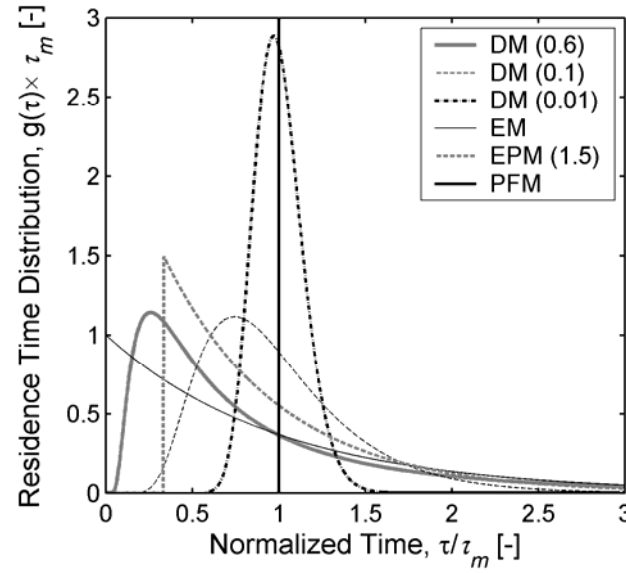


Figure 2.2. Examples of common residence time distributions, where DM is the dispersion model (dispersion parameter), EM is the exponential model, EPM is the exponential-piston flow model (piston flow parameter), and PFM is the piston flow model.  $\tau_m$  is the mean residence time and other parameters are shown in parentheses (i.e., the dispersion parameter,  $D/vx$ , and the piston flow parameter,  $\eta$ , for the dispersion and exponential-piston flow model, respectively).

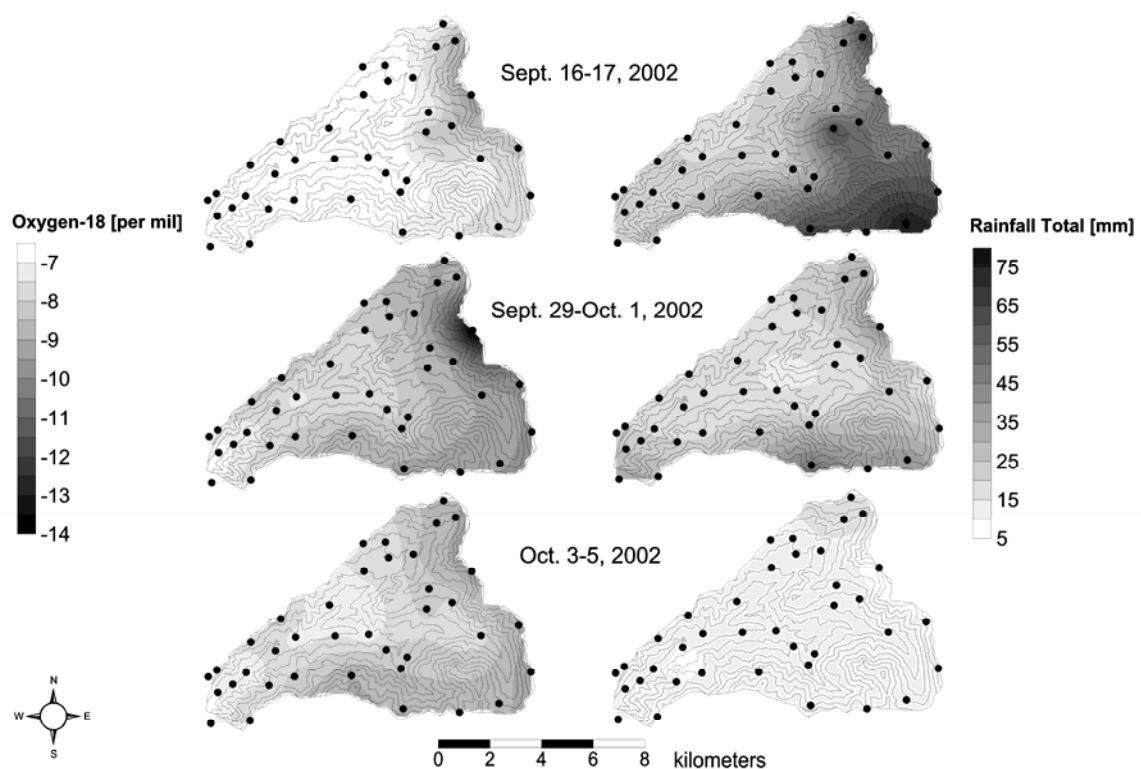


Figure 2.3. An illustration of rainfall  $\delta^{18}\text{O}$  (per mil) and rainfall depth (mm) variation of three consecutive storms in the Lookout Creek (62.4 km²) basin within the western, central Cascades of Oregon, USA. Elevations range from 430 to 1620 m. Rainfall samples were collected as bulk storm samples.

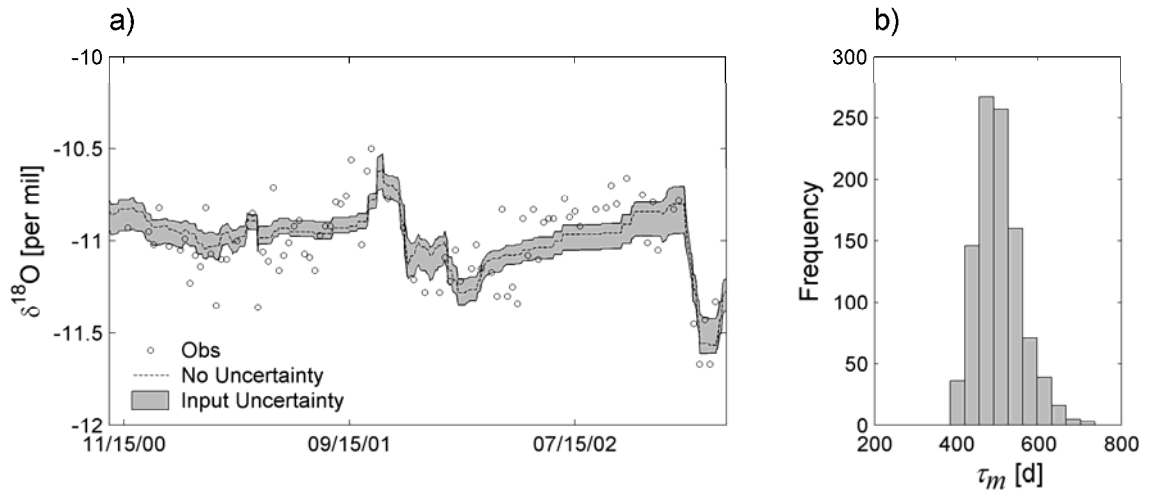


Figure 2.4. (a) An example of the effect of propagating potential input uncertainties (1000 realizations of random error  $\pm 0.75$  per mil representing elevation effects and uncharacterized spatial variation) on modeled stream flow isotopic composition and (b) estimates of the mean residence time ( $\tau_m$ ). The shaded region indicates the range of model simulations containing the input uncertainty and the dashed line is the best-fit model assuming no uncertainty.

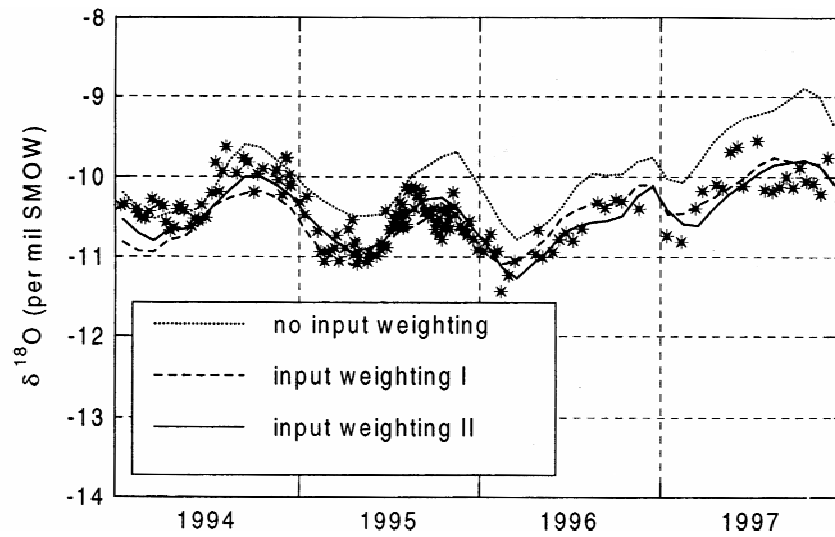


Figure 2.5. Simulated Mosnang baseflow  $\delta^{18}\text{O}$  in the Rietholtzbach catchment (Switzerland) using inputs weighted by lysimeter outflow (input weighting I) and groundwater recharge estimated from a soil water balance model, PREVAH-ETH (input weighting II) [Vitvar *et al.*, 1999].

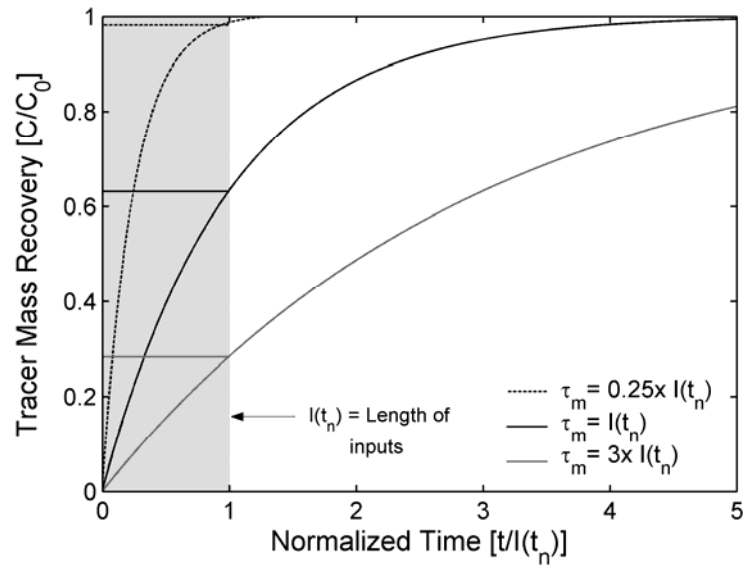


Figure 2.6. Exponential residence time distributions expressed as tracer mass recovery (cumulative RTDs). The gray shaded area hypothetically represents the length of time that inputs were measured,  $I(t_n)$ , which is also the mean residence time,  $\tau_m$ , of the solid black line. The dashed line has a mean residence time equal to 25% of the input record length and the gray line has a mean residence time equal to 3 times the input record length. The mass recovery of each system that occurs after an elapsed time equal to the input record length is shown by the horizontal lines in the gray shaded area.



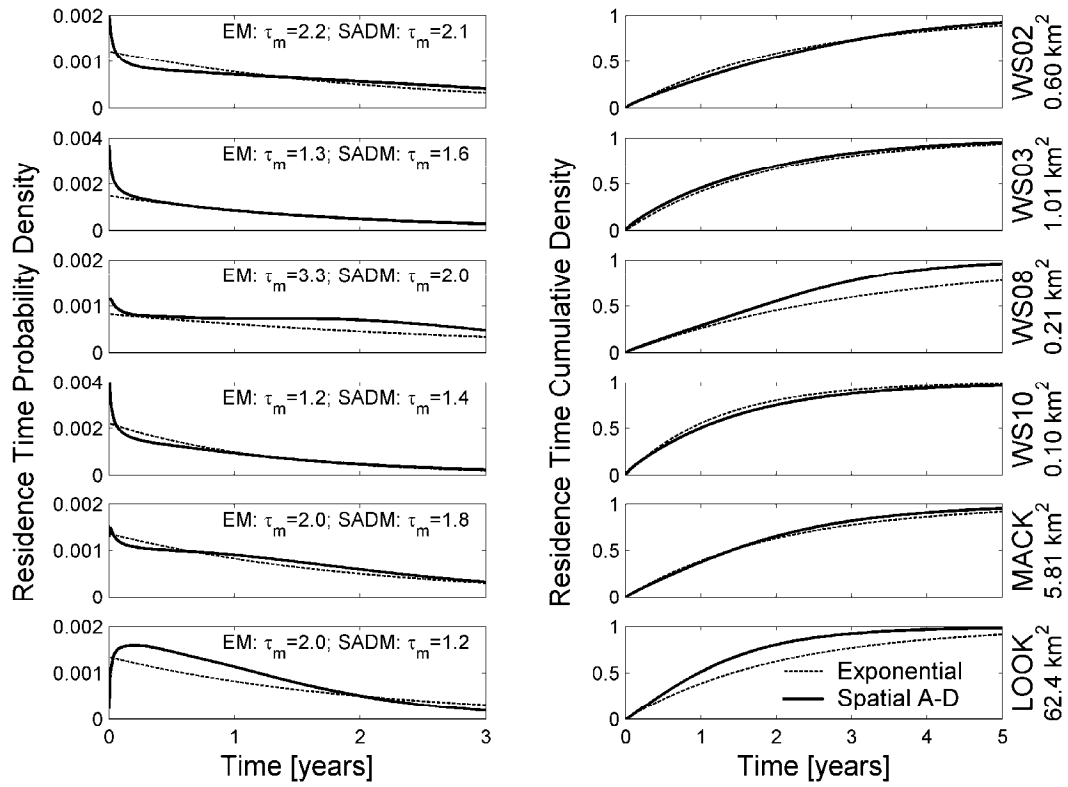


Figure 2.7. A comparison between exponential (EM) and spatially-weighted advection-dispersion models (SADM) used to interpret stream  $\delta^{18}\text{O}$  composition in 6 basins within the H.J. Andrews Experimental Forest. The spatially-weighted advection-dispersion model was based on flow path distributions computed from a catchment topography (i.e., digital elevation models), and thus more realistically captures the catchment geometry and subsurface flow system (assumed to reflect topography).

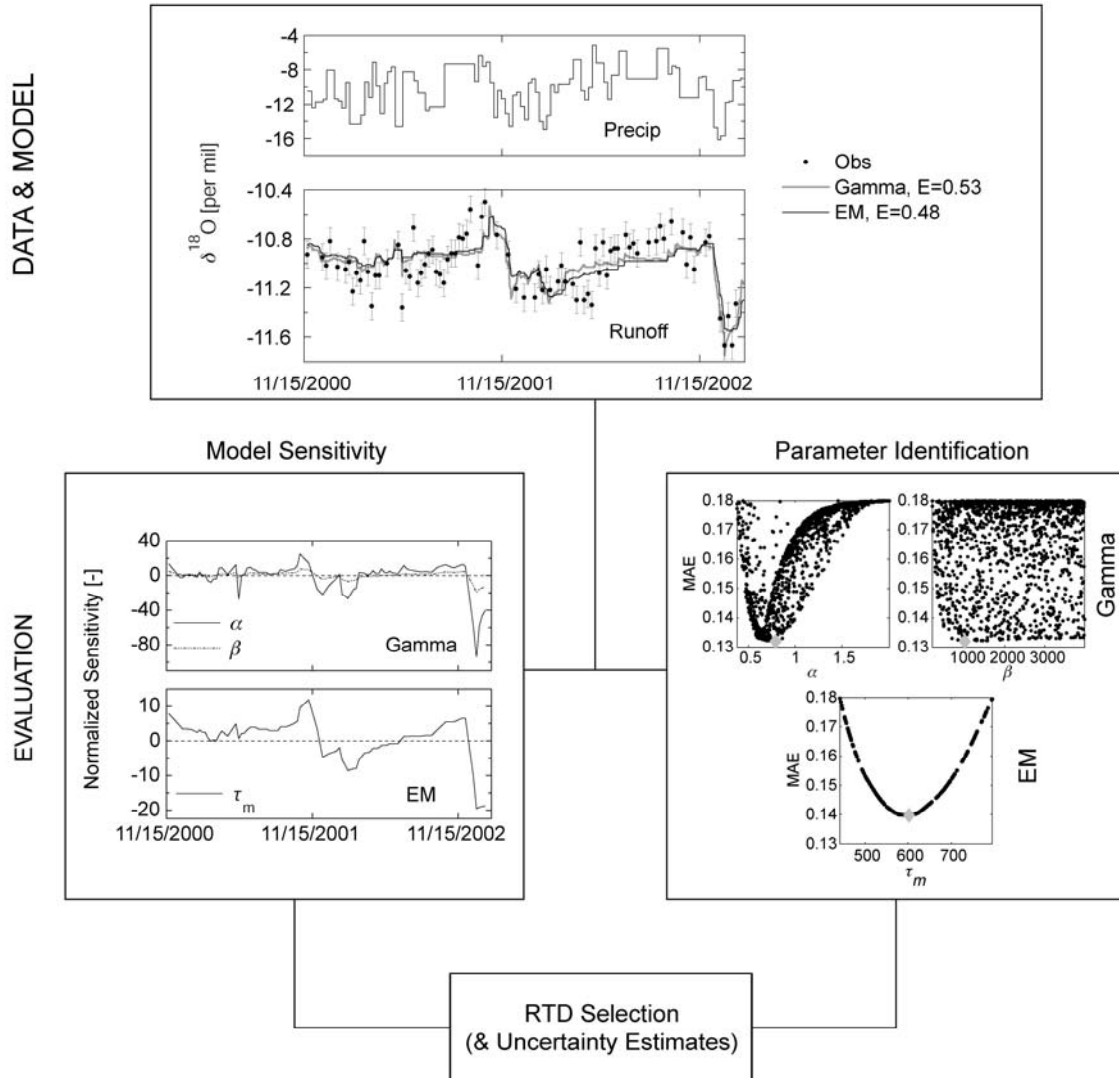


Figure 2.8. A diagram of the model evaluation and residence time distribution (RTD) selection process. The upper box contains observed data and model simulations for two RTDs (gamma and exponential). The two lower boxes illustrate the evaluation phase by examination of model sensitivity (in this case, temporal sensitivity [Knopman and Voss, 1987]) and parameter identification through scattergrams of mean absolute errors (MAE) computed from 1000 realizations of each model. The gray diamond indicates the parameter set with the lowest MAE. The final step is the selection of the best RTD given the observed data and the calculation of uncertainty estimates based on the evaluation step (e.g., confidence limits).

### **3 The role of topography on catchment-scale water residence time**

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In Review

### 3.1 Introduction

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; Sidle *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 large scale (e.g., 100 to 1000 km<sup>2</sup>) 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 m<sup>2</sup>) become effective properties determined through model calibration at larger scales.

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 [Dinçer 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.

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 meso-scale prediction where observations may be limited [*Sivapalan*, 2003]. Residence times can be used 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.*, in press]. *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.* [in press] 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? and (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 meso-scale basin (62 km<sup>2</sup>).

### 3.2 *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 3.1). The main drainage within the HJA is Lookout Creek (LOOK, 62.42 km<sup>2</sup>), 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], peakflows [*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 can be found in *Rothacher* [1967], *Jones and Grant* [1996], and *Jones* [2000].

Catchments areas (see Figure 3.1) range from 0.085 to 62.42 km<sup>2</sup> and span the climatic, geomorphic, and topographic settings found within the overall LOOK basin (see Table 3.1). 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 tuffs and breccias derived from mudflows and pyroclastic flows. In higher elevation areas (>1200 m), bedrock is composed of andesitic and 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 characteristic curves [Dyrness, 1969; Ranken, 1974; Harr, 1977]. Overland flow has not been observed 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].

### **3.3 Methodology**

#### **3.3.1 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 drain 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 and collection occurred weekly at Hi-15 during the 2001-2002 winter using a 0.25 m<sup>2</sup> 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 m<sup>2</sup> 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, weekly streamflow samples were selected to avoid events had occurred within a 24-hr window of an event based on the continuous discharge available at all sites. Thus, 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 ( $\delta^{18}\text{O}$ ) using an automated version of the  $\text{CO}_2\text{--H}_2\text{O}$  equilibration technique of Epstein and Mayeda [1953]. The  $\delta^{18}\text{O}$  values are reported in per mil (‰) relative to a standard as  $\delta^{18}\text{O} = (R_x/R_s - 1) \times 1000$ , where  $R_x$  and  $R_s$  are the  $^{18}\text{O}/^{16}\text{O}$  ratios for the sample and standard (VSMOW), respectively. The analytical precision ( $\sigma$ ) was 0.11‰ based on submitted blind duplicate samples.

### 3.3.2 *Input Characterization*

The input  $\delta^{18}\text{O}$  for each catchment was adjusted for an elevation effect [cf. Dansgaard, 1964] based on the two end-member (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, while low elevation catchments (WS02, WS03, WS09, and WS10) used the PRIMET station as the reference input signal. The

precipitation  $\delta^{18}\text{O}$  used for a basin was adjusted depending on the isotopic difference between the two precipitation stations for each collection period. This was computed as follows:

$$\delta_{in}(t) = (E_R - E_{ref})S(t) + \delta^{18}\text{O}_{ref}(t) \quad (1)$$

where  $\delta_{in}$  is the catchment specific  $\delta^{18}\text{O}$ ,  $E_R$  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  $\delta^{18}\text{O}_{ref}$  is the measured isotopic composition for the reference station. The isotopic difference term  $S$  is time dependent (i.e., varies with 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.

Inputs were then extrapolated into the past by assuming that the mean baseflow (i.e., groundwater)  $\delta^{18}\text{O}$  of each catchment reflects the long-term average input  $\delta^{18}\text{O}$  of previous precipitation. This allowed us to examine residence times that were greater than the length of time for which precipitation  $\delta^{18}\text{O}$  was measured (~1130 days). It can be shown for all sites where there is no elevation effect on the precipitation  $\delta^{18}\text{O}$ , that the long-term weighted  $\delta^{18}\text{O}$  of precipitation is approximately equal to the mean baseflow composition. Precipitation sampled at PRIMET in this study and by *Welker* [2000] had a weighted mean  $\delta^{18}\text{O}$  of -10.46‰. The baseflow mean  $\delta^{18}\text{O}$  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  $\delta^{18}\text{O}$  was -11.43‰ which was comparable to the mean baseflow  $\delta^{18}\text{O}$  in WS08 of -11.27‰.

### 3.3.3 Residence Time Modeling Theory and Approach

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  $\delta_{in}(t-\tau)$  according to their residence time distribution  $g(\tau)$  [Dinçer *et al.*, 1970; Maloszewski and Zuber, 1982; Richter *et al.*, 1993]:

$$\delta_{out}(t) = \int_0^{\infty} g(\tau) \delta_{in}(t-\tau) d\tau \quad (3)$$

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 3 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 re-expressed with both  $t$  and  $\tau$  corrected as flow time [Rodhe *et al.*, 1996]:

$$t_c = \int_{t_0}^t Q(t) dt / \bar{Q} \quad (4)$$

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 Eqn. 3 and obtained similar

fits to our stream isotope data and essentially equivalent residence time distributions using both approaches. *Kirchner et al.* [2000; 2001] also found that a similar time transformation yielded equivalent results to Eqn. 3. Therefore, we used the strict time-based approach since interpretation is more straightforward.

The convolution equation (3) 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]:

$$\delta_{out}(t) = \frac{\int_0^{\infty} g(\tau)w(t-\tau)\delta_{in}(t-\tau)d\tau}{\int_0^{\infty} g(\tau)w(t-\tau)d\tau} \quad (5)$$

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 rates were used since the seasonality of precipitation and recharge are strongly correlated at HJA. From Eqn. 5 (and 3) it is clear that  $g(\tau)$  must sum to unity to conserve mass.

The travel time or residence time distribution (RTD or  $g(\tau)$ ) describes 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, then the tracer RTD is equal to the water RTD. 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; *Etcheverry and*

*Perrochet, 1999; Rodhe et al., 1996*]. RTDs used in Eqns. 3 and 5 are time-invariant, spatially-lumped characteristics of the catchment and thus describe average catchment behavior.

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 stormflow 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*].

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 3.2. 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 [*Haitjema, 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 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 (Eqn. 3) in the frequency domain), they found that the shape parameter  $\alpha$  for the gamma distribution (see Table 3.2) 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 3.2, model 6) and two exponential distributions in parallel [as described by *Weiler et al., 2003*].

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  $\delta^{18}\text{O}$ . Parameter estimate standard deviations ( $\sigma_p$ ) were computed from the variance-covariance matrix following a first-order linear approximation method [*Donaldson and Schnabel, 1987; Ratkowsky, 1990*]. For purposes of model comparison, we used the Nash-Sutcliffe [1970] efficiency ( $E$ ) and root mean square error corrected (RMSE) for the number of parameters estimated. 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.

### 3.3.4 Topographic Analysis

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. Based on 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.

An accumulated area grid was computed using the methods of McGlynn and Seibert [2003] from which flow path length and flow path gradient distributions were determined for each catchment. Likewise, the local sub-catchment area for each stream segment (i.e., flagged stream cells) was computed to determine the sub-catchment area distribution for each basin [McGlynn and Seibert, 2003]. Other basic topographic attributes were computed such as the mean slope, hysometric integral [Chorley *et al.*, 1985], and topographic,  $\ln(\alpha/\tan\beta)$ , index [Beven and Kirkby, 1979]. We then compared these descriptions of internal catchment form at each catchment scale to estimated mean residence time to explore possible relationships with catchment topographic organization.

## 3.4 Results

### 3.4.1 Spatial and Temporal Isotopic Patterns of Precipitation and Streamflow

Precipitation amounts were generally similar between Hi-15 and PRIMET (p value=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 (Nov. to Apr.) average weekly amounts were 68 mm and summer (May to Oct.) average weekly amounts were 24 mm. Both sites had significant seasonal patterns of  $\delta^{18}\text{O}$  with approximate annual periodic fluctuations ranging over of 8‰ for the years 2000 and 2002 (Figure 3.2). 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  $^{18}\text{O}$  than PRIMET, on average by -0.83‰ ( $\pm 0.39\%$ ).

Spatial variations in rainfall amount and isotopic composition also indicated strong elevation effects (Figure 3.3). The largest storm sampled (9/16-17) 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 9/29-10/1 and 10/3-5, respectively) and had less overall variation (range = 14.7 to 49.1 mm and 5.1 to 18.2 mm for 9/29-10/1 and 10/3-5, 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  $\delta^{18}\text{O}$  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 (Eqn. 1).

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*]. This 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 0.080‰. 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 3.2). Also, cold air drainage, which has a tendency to affect the PRIMET station, (Chris Daly, personal communication) 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*].

Snowmelt sampled at Hi-15 between 12/11/2001 and 4/30/2002 showed progressive enrichment in  $^{18}\text{O}$  (approximately 0.02‰ per day for the period 1/2/2002 to 4/30/2002) throughout the melt season (see Figure 3.2). Snowmelt was not sampled during the 2000-2001 melt season; however, the snowpack was approximately 20% less than the long-term mean that season. Snowpack persistence at PRIMET rarely exceeded 2 weeks during the study period.

The stream  $\delta^{18}\text{O}$  composition generally reflected the temporal pattern of the precipitation  $\delta^{18}\text{O}$  composition; however, the signals were significantly damped (Figure 3.2). The  $\delta^{18}\text{O}$  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).

### 3.4.2 Residence Time Modeling

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 3.3). However, only the exponential distribution performed consistently well for all basins (Figure 3.4). 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 some 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 3.3). The shape parameter  $\alpha$  optimized for the gamma distribution was approximately 1 for all simulations given the large parameter estimate confidence limits, which is equivalent to an exponential distribution (see Table 3.2). 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 3.3). 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.

The simulations shown in Figure 3.4 are the best performing exponential models overall. More importantly, they are among the simplest since only one distribution parameter was optimized (i.e.,  $\tau_m$ ). 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 determined by the temporal nature of  $\tau_m$  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 3.3). 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  $\tau_m$  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 3.5). The Nash-Sutcliffe objective measure [*Nash and Sutcliffe*, 1970] 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 Eqn. 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 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 using other residence time models were used. The effective recharge elevation parameter only changes the input composition to reflect the observed isotopic elevation effects (Figure 3.2).

The RTDs in Figure 3.6 illustrate the diverse transport behavior within the overall LOOK drainage. These distributions indicate the relative memory of the catchments to past inputs; thus, reflect how long these catchment store and release water or soluble 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.

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 3.6 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 1.3.2). For example, 39% of the

tracer mass in WS08 originated prior to our observations. Cumulative residence time distributions shown in the inset plot of Figure 3.6 further illustrate this point.

### 3.4.3 Residence Time and Topographic Analysis

Catchment area showed no apparent relationship to the estimated mean residence times ( $\tau_m$ ) ( $r^2 < 0.01$ ) (Figure 3.7a). The two largest basin scales, MACK (5.81 km<sup>2</sup>) and LOOK (62.42 km<sup>2</sup>), had younger  $\tau_m$  than WS02 (0.601 km<sup>2</sup>) and WS08 (0.214 km<sup>2</sup>), while catchments with the youngest  $\tau_m$  were the smallest basins (WS09 and WS10, 0.085 and 0.102 km<sup>2</sup>, respectively). Other topographic indices were regressed against the mean residence time, including the accumulation of sub-catchment areas (e.g., median sub-catchment area,  $r^2 < 0.01$ ), the hypsometric integral ( $r^2 = 0.36$ ), and the mean topographic index ( $r^2 = 0.85$ ). 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 3.7; Note: 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  $\tau_m$  ( $r^2 = 0.79$ ).

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. Figure 3.7b, 3.7c, and 3.7d show the medians of flow path length ( $r^2 = 0.72$ ), flow path gradient ( $r^2 = 0.64$ ), and their ratio (*LG ratio*) ( $r^2 = 0.91$ ) compared to  $\tau_m$ . The correlation between  $\tau_m$

and the *LG* ratio remains high even if WS08 were removed ( $r^2=0.71$ ) considering that its  $\tau_m$  estimate likely contains the most uncertainty (i.e.,  $2\sigma_p = 1.28$  y and only 61% of the tracer mass can be accounted for by the model within the time period of measurements).

### 3.5 Discussion

#### 3.5.1 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 km<sup>2</sup>) 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 km<sup>2</sup> 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 sub-basin 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 3.3). 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 in Kirchner [2000]. However, the confidence limits (Table 3.3) 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  $\delta^{18}\text{O}$  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 3.5).



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].

### 3.5.2 *The Topographic Relationship*

Results from some studies and reviews [*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.*, in press], 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 *Wolock et al.* [1997], which suggested that the spatial pattern of stream geochemistry across basin scale was largely controlled by the increase in contact time (a residence time surrogate) with basin scale.

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 spatial variability of 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 3.7). Buttle *et al.* [2001] and Rodhe *et al.* [1996] both found weak correlations between groundwater residence times in various catchment positions and the  $\ln(\alpha/\tan\beta)$  index, suggesting similar behavior.

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 sub-catchments that drain to the stream channels (an indication of the portion of area that accumulates as hillslope), but not the true catchment area. Thus, catchment area did not accumulate similarly across scales or between catchments of similar size. McGlynn *et al.* [2003] suggested that the distribution of sub-catchment areas might be more useful than total catchment area for evaluating watershed function. While, our analysis did not show a significant relationship with median sub-catchment area, the *LG* ratio also suggests that the hillslope and channel network structure are more important controls on transport than total catchment area. The flow path length and gradient distribution reflects the hydraulic

driving force of catchment-scale transport (i.e., Darcy's law). Considering the empirical nature of these results and that mean and median are simple characteristics of the distributions, it is clear that some description of topography provides a first-order control on flow processes and transport. The nature of the  $LG$  ratio and  $\tau_m$  relationship is not expected to be similar at other sites. Rather, the slope of the line is expected to change reflecting the relative role of topography and that perhaps other descriptions (e.g., sub-catchment area accumulation) are more useful at other sites and regions that show little change in hillslope lengths and gradient. For example, in a recent study by *Rodgers et al.* [in press],  $\tau_m$  appears to be related to a combination of topography and soil type.

Our observation of strong topographic control on residence time suggests that the HJA flow system is relatively shallow and dominated by topography. Notwithstanding, the residence time results suggest that average storage significantly exceeds approximated average soil depths ( $\tau_m$  = volume of mobile water (i.e., storage) divided by 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 topographic variation at the HJA also reflects differences in the geology and geologic history. Lower elevation basins (WS02, WS03, WS09, WS10) are generally underlain by the highly weathered Oligocene-lower Miocene volcanticlastic rocks. The

topography in these areas is characterized by steeply dissected short hillslopes, while other areas that have been glaciated and/or contain earthflows (e.g., WS08), generally have gentle topography and longer hillslopes. Therefore, topographic relationships presented herein also reflect geologic features, which were also expected influence the RTDs.

### 3.5.3 *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 multi-scale 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 meso-scale 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 meso-scale 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 multi-criteria 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].

### **3.6 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 meso-scale. Results from this study suggest that tracers might help bridge the gap between small basins and the meso-scale 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.

### 3.7 Acknowledgments

This work was supported through funding from the National Science Foundation (grant DEB 021-8088 to the Long-Term Ecological Research Program at the H. J. Andrews Experimental Forest) and Department of Forest Engineering at Oregon State University. We thank C. Creel, G. Downing, and J. Moreau for assistance in the field; D. Henshaw for access to meteorological and streamflow data from the FSDB; R. Haggerty for suggestions on parameter confidence limits and J. Jones for helpful comments on an earlier draft.

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Table 3.1. Geologic and geomorphic catchment descriptions.

Catchment	Area [km <sup>2</sup> ]	Mean Slope [°]	Minimum Elevation		Maximum Elevation [m]	Geologic/Geomorphic Description <sup>a</sup>
			[m]	[m]		
WS02	0.601	27	548	1070	97% Steep volcanics, 3% fractured andesitic/basaltic lava flows & soils <1 m	
WS03	1.011	26	418	1080	68% Steep volcanics with <1 m soils, 22% Earthflow with >3 m soils, 10% fractured andesitic/basaltic lava flows	
WS08	0.214	15	993	1170	55% Bench volcanics and glaciated till/colluvium, 45% Earthflow with >3 m soils, 24% glaciated till/colluvium	
WS09	0.085	31	432	700	99% Steep volcanics with <1 m soils	
WS10	0.102	29	473	680	92% Steep volcanics, with basaltic/rhyolitic dikes & 1-3 m soils	
MACK	5.81	25	758	1610	82% Steep volcanics with <1 m soils, 18% fractured andesitic/basaltic lava flows	
LOOK	62.42	20	428	1620	All of the above including large alluvial stream terraces, ca. 1-3 m soils	

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

Table 3.2. Descriptions of residence time distributions.

Model	Residence time distribution, $g(\tau)$	Parameters	Mean residence time <sup>†</sup>
1. Exponential <sup>a</sup>	$\tau_m^{-1} \exp(-\tau/\tau_m)$	$\tau_m$	$\tau_m$
2. Exponential-piston flow <sup>a</sup>	$\begin{cases} \left(\frac{\tau_m}{\eta}\right)^{-1} \exp\left(-\frac{\eta\tau}{\tau_m} + \eta - 1\right) \\ \text{for } \tau \geq \tau_m(1 - \eta^{-1}) \\ 0 \text{ for } \tau < \tau_m(1 - \eta^{-1}) \end{cases}$	$\tau_m, \eta$	$\tau_m$
3. Dispersion <sup>a</sup>	$\left(\frac{4\pi D_p \tau}{\tau_m}\right)^{-1/2} \tau^{-1} \times \exp\left[-\left(1 - \frac{\tau}{\tau_m}\right)^2 \left(\frac{\tau_m}{4D_p \tau}\right)\right]$	$\tau_m, D_p^{\ddagger}$	$\tau_m$
4. Gamma <sup>b</sup>	$\frac{\tau^{\alpha-1}}{\beta^\alpha \Gamma(\alpha)} \exp(-\tau/\beta)$	$\alpha, \beta$	$\alpha\beta$
5. Two parallel linear reservoirs <sup>c</sup>	$\frac{\phi}{\tau_f} \exp\left(-\frac{\tau}{\tau_f}\right) + \frac{1-\phi}{\tau_s} \exp\left(-\frac{\tau}{\tau_s}\right)$	$\tau_f, \tau_s, \phi$	--
6. Power-law <sup>d</sup>	$\frac{\tau^k}{\Gamma(1-k)}$	$k$	--

<sup>†</sup>No characteristic residence time is associated with model 6, model 5 was calculated numerically by the 1<sup>st</sup> moment

<sup>‡</sup> $D_p = 1/\text{Peclet number}$

<sup>a</sup>*Maloszewski and Zuber* [1982]

<sup>b</sup>*Kirchner et al.* [2001]

<sup>c</sup>*Weiler et al.* [2003]

<sup>d</sup>*Schumer et al.* [2003]

Table 3.3. Residence time modeling results<sup>a</sup>.

Site	Exponential				Gamma				Two parallel linear reservoirs				Power-law			
	$E_R (\pm 2\sigma_p)$ <sup>b</sup> [m]	$\tau_m (\pm 2\sigma_p)$ <sup>b</sup> [y]	$E$	RMSE [%]	$\alpha (\pm 2\sigma_p)$ [-]	$\beta (\pm 2\sigma_p)$ [y]	$E$	RMSE [%]	$\tau_f (\pm 2\sigma_p)$ <sup>c</sup> [y]	$\tau_s (\pm 2\sigma_p)$ <sup>c</sup> [y]	$\phi^c$ [-]	$E$	RMSE [%]	$k (\pm 2\sigma_p)$ [-]	$E$	RMSE [%]
WS02	647 ( $\pm 36$ )	2.2 ( $\pm 0.56$ )	0.45	0.11	0.78 ( $\pm 0.21$ )	5.5 ( $\pm 7.55$ )	0.48	0.10	0.3 ( $\pm 0.29$ )	16.5	0.08	0.49	0.10	0.38 ( $\pm 0.05$ )	0.47	0.11
WS03	594 ( $\pm 42$ )	1.3 ( $\pm 0.31$ )	0.48	0.17	0.74 ( $\pm 0.19$ )	3.4 ( $\pm 3.60$ )	0.53	0.16	0.3 ( $\pm 0.24$ )	10.8	0.16	0.52	0.16	0.48 ( $\pm 0.05$ )	0.45	0.16
WS08	994 ( $\pm 32$ )	3.3 ( $\pm 1.28$ )	0.40	0.09	0.96 ( $\pm 0.23$ )	3.6 ( $\pm 2.87$ )	0.41	0.09	0.5	7.0	0.08	0.40	0.09	0.32 ( $\pm 0.11$ )	0.37	0.09
WS09	432 ( $\pm 50$ )	0.8 ( $\pm 0.18$ )	0.46	0.25	0.92 ( $\pm 0.22$ )	1.0 ( $\pm 0.60$ )	0.46	0.25	0.3 ( $\pm 0.20$ )	21.9	0.24	0.60	0.22	0.53 ( $\pm 0.08$ )	0.40	0.26
WS10	474 ( $\pm 47$ )	1.2 ( $\pm 0.29$ )	0.49	0.19	0.76 ( $\pm 0.18$ )	2.6 ( $\pm 2.12$ )	0.51	0.19	0.3 ( $\pm 0.30$ )	18.7	0.20	0.53	0.19	0.49 ( $\pm 0.07$ )	0.43	0.21
MACK	1010 ( $\pm 28$ )	2.0 ( $\pm 0.49$ )	0.54	0.12	0.97 ( $\pm 0.17$ )	2.2 ( $\pm 1.15$ )	0.54	0.12	0.3	2.3 ( $\pm 1.84$ )	0.04	0.54	0.12	0.37 ( $\pm 0.08$ )	0.42	0.14
LOOK	916 ( $\pm 48$ )	2.0 ( $\pm 1.00$ )	0.32	0.11	1.23 ( $\pm 0.39$ )	1.1 ( $\pm 0.98$ )	0.36	0.11	0.4	2.0 ( $\pm 4.91$ )	0.00	0.32	0.11	0.30 ( $\pm 0.18$ )	0.19	0.12

<sup>a</sup>The best fit parameter value, its associated 95% confidence limits (i.e.  $2\sigma_p$ ), measure of efficiency ( $E$ ), and root mean square error (RMSE) are listed for each model.

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

<sup>c</sup>If estimates of the confidence limits are not shown they were  $>5$  times the parameter estimate; thus, the given parameter estimate was ill-determined.

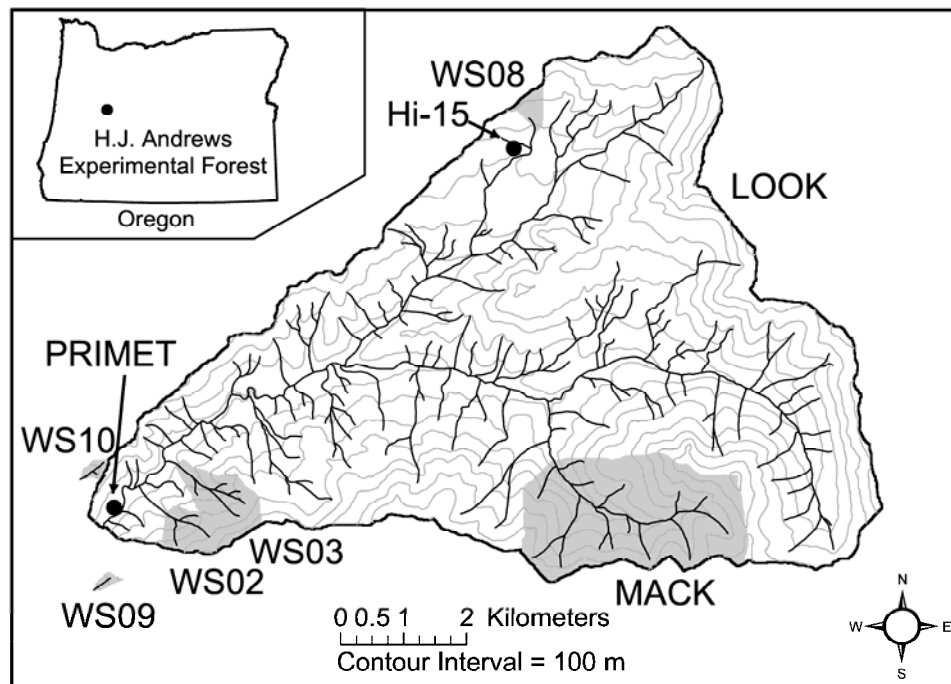


Figure 3.1. Map of the H.J. Andrews Experimental Forest showing the locations of the study catchments.



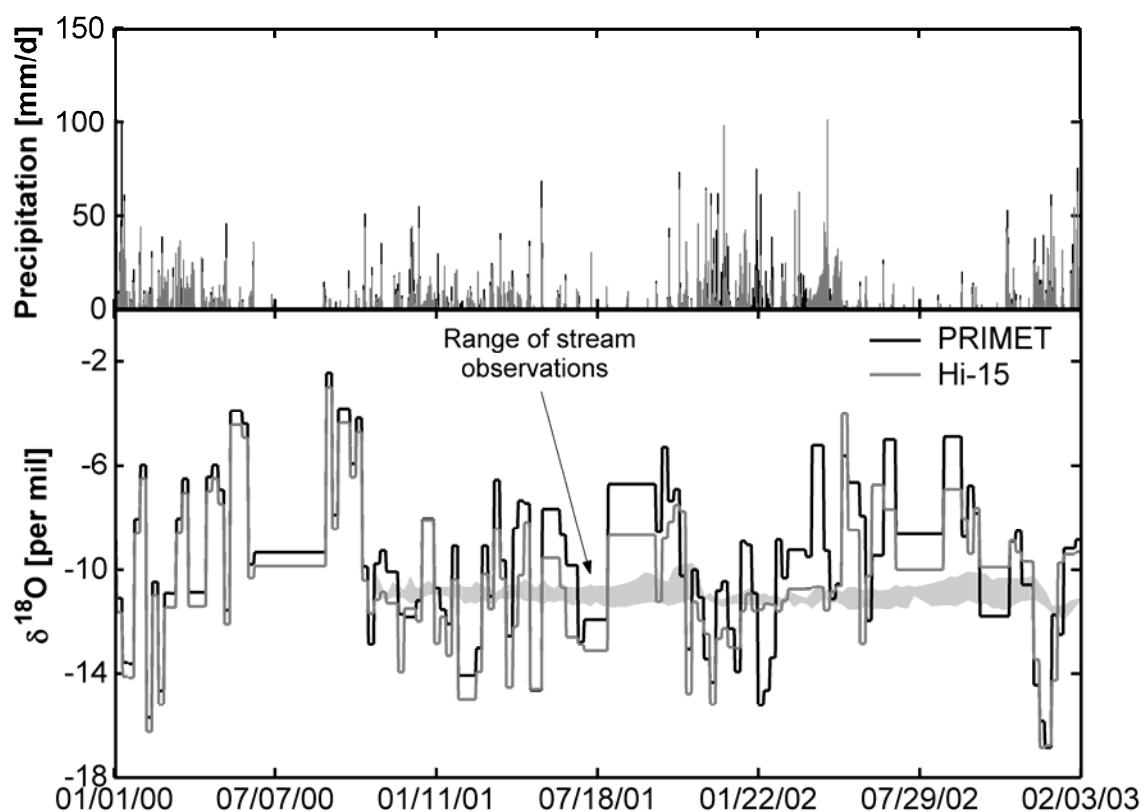


Figure 3.2. Daily precipitation and weekly  $\delta^{18}\text{O}$  measured at PRIMET (430 m) and Hi-15 (922 m) meteorological stations. The shaded area shows that range of measured streamflow  $\delta^{18}\text{O}$  for all catchments.

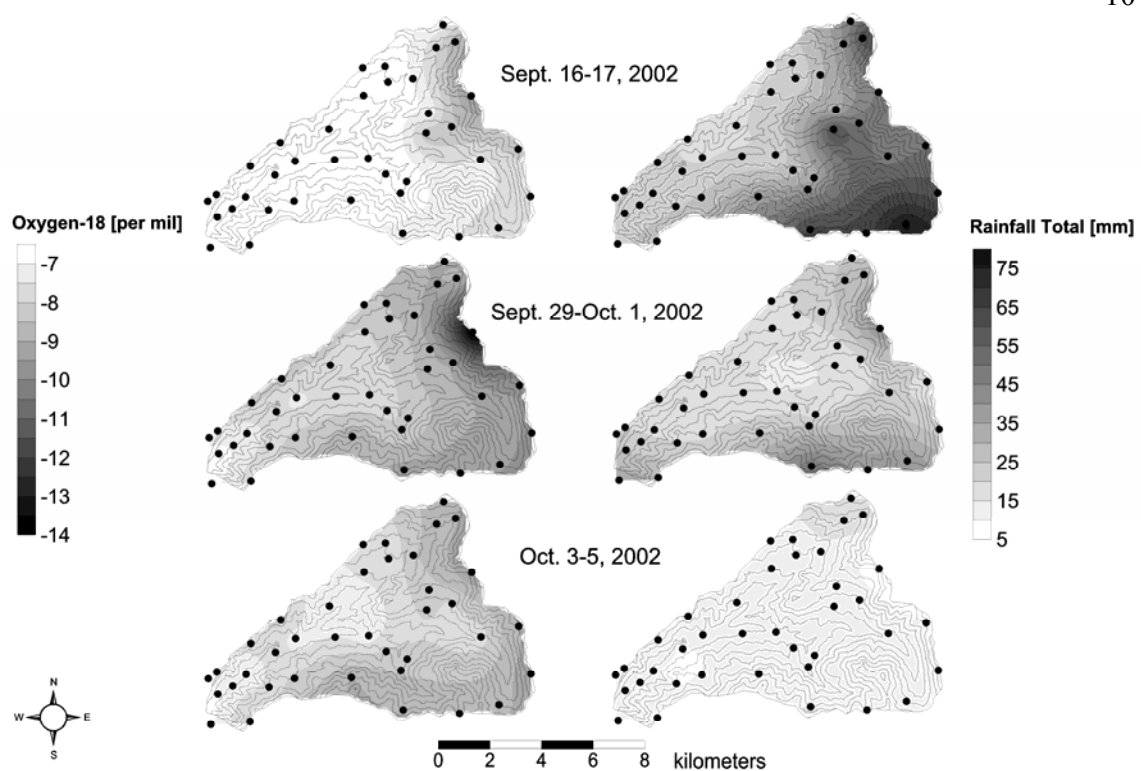


Figure 3.3. Spatial patterns of total storm rainfall and  $\delta^{18}\text{O}$  for three synoptically sampled events during the fall 2002. The black circles indicate the location of bulk samplers used to collect rainfall.

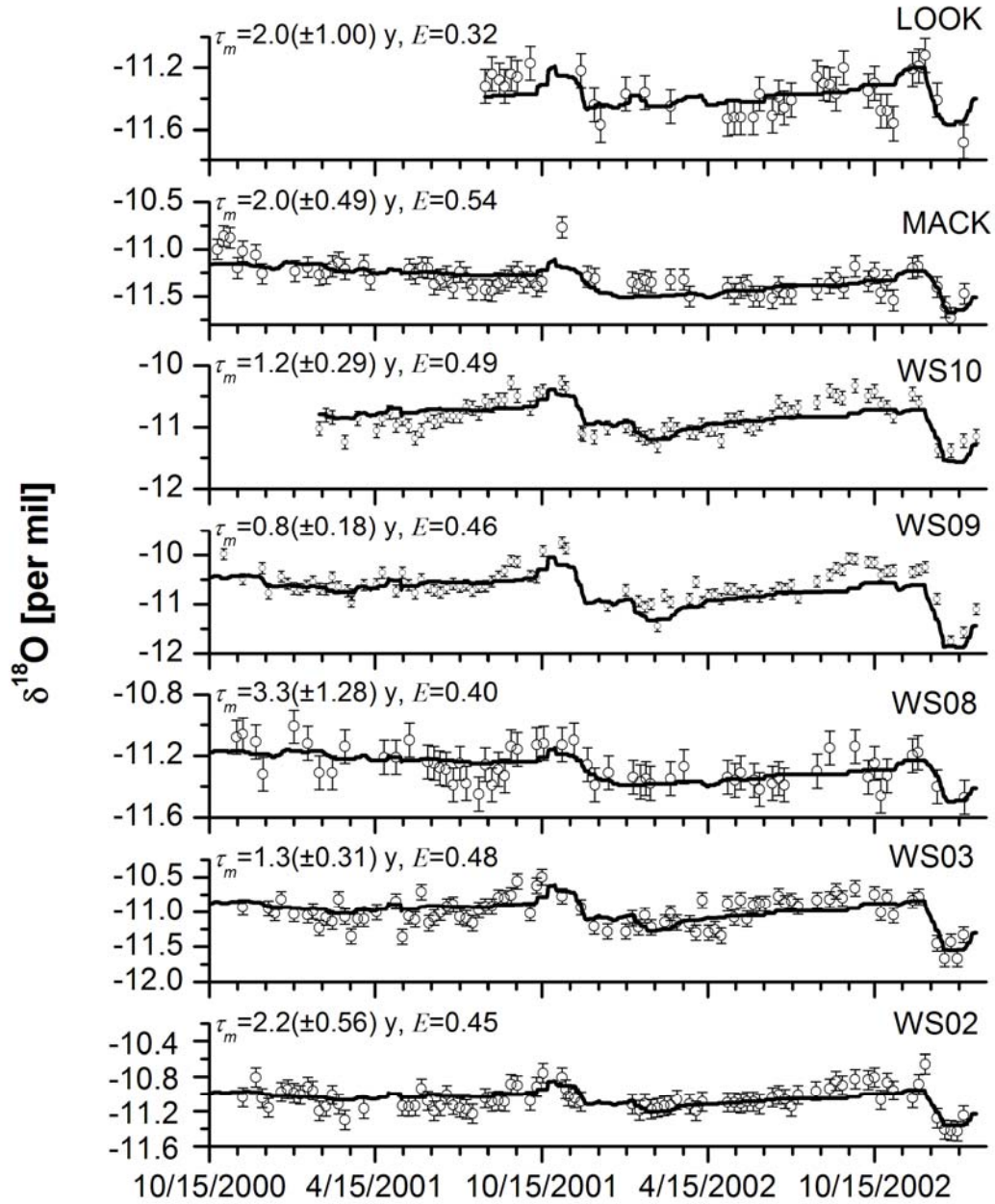


Figure 3.4. Measured and modeled  $\delta^{18}\text{O}$  for each catchment. Estimated mean residence times ( $\tau_m$ ) are shown with 95% confidence limits ( $2\sigma_p$ ) in parentheses. Nash-Sutcliffe efficiency measures ( $E$ ) [Nash and Sutcliffe, 1970] are shown for model simulation comparisons. Error bars indicate the analytical reproducibility for  $\delta^{18}\text{O}$  measurements.

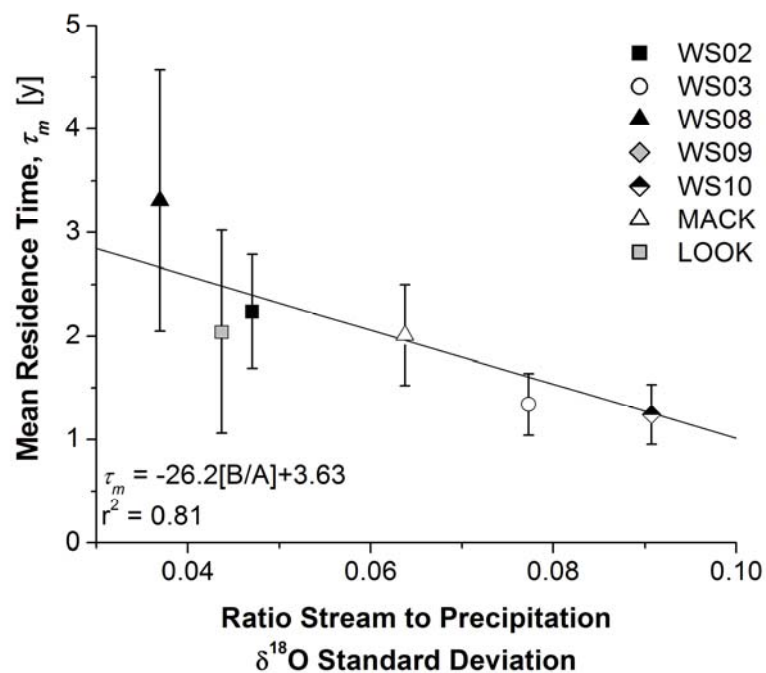


Figure 3.5. The relationship between mean residence time ( $\tau_m$ ) and ratio of the standard deviations of  $\delta^{18}\text{O}$  measurements of stream water (B) to precipitation (A). Error bars indicate the 95% confidence limits ( $2\sigma_p$ ) of the  $\tau_m$  parameter estimates.

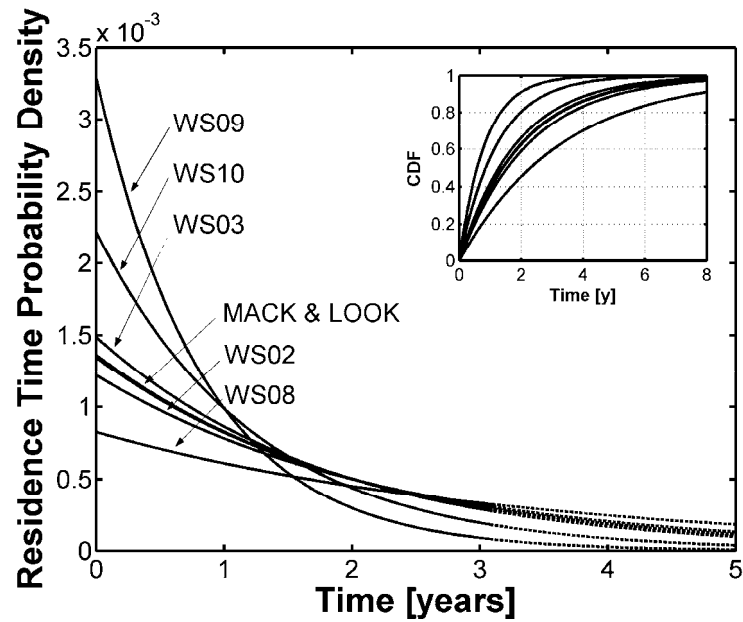


Figure 3.6. Residence time distributions based on best parameter estimates for each catchment. The solid line designates the length of the study period and the inset figure shows the cumulative residence time distributions (CDF) that can be interpreted as mass recovery from an instantaneous, uniform tracer addition.

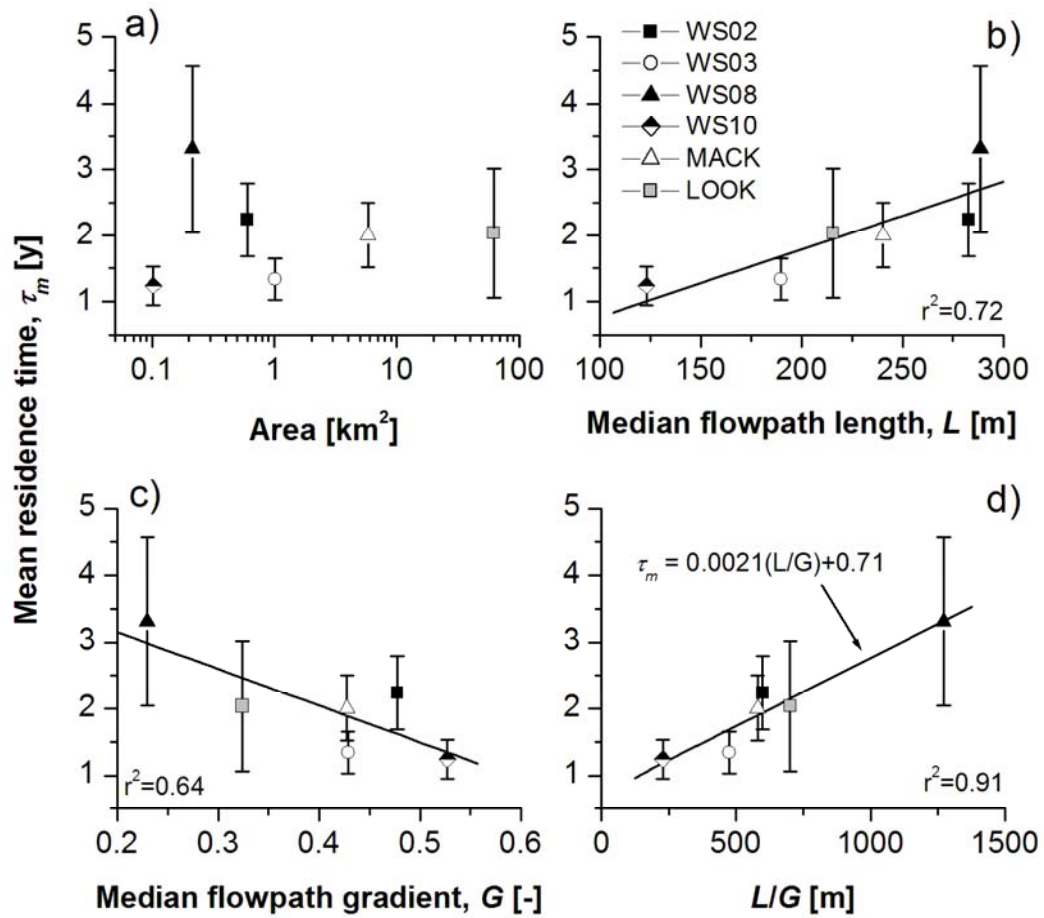


Figure 3.7. The relationships between mean residence time estimated by modeling  $\delta^{18}\text{O}$  variations in stream water (Eqn. 5) and (a) catchment area, (b) median flowpath length ( $L$ ), (c) median flowpath gradient ( $G$ ), and (d) the ratio of median flowpath length to median flowpath gradient ( $L/G$ ). Median flowpath values were determined from all potential flowpaths defined by a DEM analysis. Error bars indicate the 95% confidence limits ( $2\sigma_p$ ) of the  $\tau_m$  parameter estimates.

#### **4 The role of hillslopes on catchment response: connectivity, flow path, and residence time**

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#### 4.1 Introduction

Although it is generally acknowledged that subsurface flow dominates runoff in forested catchments, specific pathways, residence times and sources of water often remain unclear [Bonell, 1998]. In particular, the processes that provide hillslope-catchment hydrological linkages are still not well understood. Recent studies have shown that the hillslope connection depends on wetness, soil properties and surface and bedrock topography [Freer *et al.*, 1997; Sidle *et al.*, 2000; Buttle *et al.*, 2004] and in some cases, hillslopes only rarely connect to the stream environment [Hooper, 2001]. The hydrologic coupling between hillslopes and catchments is prerequisite for the delivery of biogeochemical solutes downslope to the stream [Creed *et al.*, 1996; Hooper *et al.*, 1998; Buttle *et al.*, 2001; Stieglitz *et al.*, 2003]. Reconciling these connections at the catchment scale is an arduous task since hillslope contributions are often initiated after exceeding a storage threshold [Tani, 1997; Buttle *et al.*, 2004; Kim *et al.*, 2004] or they are obscured by throughflow spatial variability [Woods and Rowe, 1996] and by the presence of other landscape elements such as riparian zones [McGlynn and McDonnell, 2003]. Sivapalan [2003] has made a plea to experimentalists for the simplification of hillslope process complexity and focus away from the detailed process heterogeneity towards a definition of common features that link process descriptions at hillslope and watershed scales.

This study is an attempt to whittle down the process complexity at an intensive experimental site to define clear hillslope-catchment process linkages. We investigate runoff dynamics and hillslope connectivity in a catchment with an unambiguous hillslope signal, where the riparian zone has been largely removed via past major debris flows.



Therefore, the catchment runoff response expresses an unadulterated response of multiple hillslopes. In seeking to understand hillslope-catchment connectivity and to evaluate its temporal evolution, we focus on a planar sideslope during a wet-up period that begins with extremely dry soil conditions and progressively increases in wetness.

We base our observations and constrain our conceptualization on hydrometric, stable isotope, and applied tracer responses following recommendations by *Bonell* [1998] and *Burns* [2002] and compute residence time distributions for various runoff components. These data resources allow us to reject many possible behaviors to decipher and explore the physical controls on runoff generation and hillslope-catchment connectivity on a well-studied hillslope [i.e., *Harr*, 1977]. We test the following null hypotheses: 1) stream discharge is linearly related to hillslope discharge, 2) hillslopes are not capable of transporting solutes (tracer) to the stream from upslope areas during a storm event, 3) event water contributions are similar for the hillslope and catchment, and 4) hillslope residence time increases downslope and is similar to the stream when it reaches the slope base.

#### **4.2 Site Area and Methods**

The study was conducted in Watershed-10 (WS10, 10.2 ha) at the H.J. Andrews Experimental Forest (HJA) in the west-central Cascade Mountains of Oregon, USA (44.2° N, 122.25° W) (Figure 4.1). WS10 was the location of intensive forest ecological research as part of the U.S. International Biological Program's Coniferous Forest Biome project [*Sollins et al.*, 1980; *Sollins et al.*, 1981; *Gholz et al.*, 1984; *Triska et al.*, 1984] and is currently part of the NSF Long-term Ecological Research (LTER) program at the

HJA. Elevations range from 473 m at the flume to 680 m at the catchment divide.

Annual precipitation is 2220 mm (averaged from 1990 to 2002), about 80% of which falls between October and April during frequent, long duration, low to moderate intensity frontal storms. The climate is Mediterranean with strong contrasts between summer and winter precipitation amounts [Greenland, 1994]. The catchment experiences a gradual wet-up period from about October to December and thereafter maintains very high wetness until late spring. Snow accumulations are common, but seldom persist longer than 1-2 weeks and generally melt within 1-2 days. No major snow accumulation was observed during this study. On average, 56% (28 to 76%) of the annual precipitation becomes runoff. Summer low flows are approximately  $0.2 \text{ L s}^{-1}$  and typical winter storms obtain peak flows of approximately  $40 \text{ L s}^{-1}$  ( $1.4 \text{ mm h}^{-1}$ ). The largest storm on record produced a peak flow of  $246 \text{ L s}^{-1}$  ( $8.7 \text{ mm h}^{-1}$ ). The vegetation is dominated by a naturally regenerated second growth Douglas-fir (*Pseudotsuga menziesii*) stand resulting from a 1975 clear-cut harvest.

The catchment is steep with slopes ranging from 30 to over 45° and contains residual and colluvial clay loam soils derived from andesitic tuffs (30%) and coarse breccias (70%) comprising the Little Butte Formation formed as the result of ash fall and pyroclastic flows from Oligocene-Early Miocene volcanic activity [Swanson and James, 1975; James, 1978]. Average soil depth is approximately 130 cm. Surface soils are well aggregated; however, lower depths (70-110 cm) exhibit more massive blocky structure with less aggregation than surface soils [Harr, 1977]. Beneath the weakly developed A and B horizons is partially weathered parent material (saprolite) ranging in thickness from 1 to 7 meters (~3.7 m on average) [Harr and McCorison, 1979; Sollins et al., 1981].

The catchment experiences periodic debris flows (e.g., as recently 1986 and 1996) that maintain a stream channel that is scoured to bedrock over the lower 60% of its length. The upper portion of the channel contains a narrow (<1 m), and in some cases, deeply incised near-stream area with frequent sections of exposed bedrock. In general, the channel width ranges from 0.25 m in the upper reaches to 1.0-1.5 m at the catchment's base [Triska *et al.*, 1984]. The overall slope of the stream channel is 24°. Thus, WS10 represents a catchment dominated by hillslopes with negligible storage of water in riparian areas. Well defined seeps have been identified flowing from the base of the hillslope soils into the stream channel [Harr, 1977; Triska *et al.*, 1984]. These seeps are highly localized zones of saturated soil related to the microtopography of the unweathered bedrock near the stream or to the presence of small vertical, andesitic dikes approximately 5 meters wide, located within the basin [Swanson and James, 1975; Harr, 1977]. While the seepage areas remain isolated during and between events, we observed a linear increase in discharge downstream during a lowflow stream tracer experiment, suggesting a uniform contribution of hillslopes within the catchment.

Our hillslope study area was located on the south aspect of WS10, 91 m upstream from the stream gauging station (Figure 4.1). This site was re-established from early 1970s-era benchmark studies [Harr and Ranken, 1972; Harr, 1977; Sollins and McCorison, 1981; Sollins *et al.*, 1981]. The slope is representative of the two main planar hillslopes that compose the overall quintessential v-shaped catchment (WS10). The 125 m long stream-to-ridge slope is slightly convex and its gradient averages 37°, ranging from 27° near the ridge to 48° adjacent to the stream. Elevation ranges from 480 to 565 m. Harr and Ranken [1972] excavated eleven soil pits on the study slope (Figure

4.1) and collected 452 soil cores from the pits. The cores were analyzed for hydrologic properties including hydraulic conductivity, porosity, pore-size distribution, moisture characteristics, and stone content [Ranken, 1974; Harr, 1977]. Hydraulic conductivity is sufficiently high that only the stream channel and bedrock surfaces produce overland flow. The main rationale for selecting this study slope was the richness of local data resources from these previous studies and the ability to be able to build on this knowledge-base, specifically the studies by Harr and Ranken.

#### 4.2.1 Instrumentation

A 10 m long trench was constructed to measure subsurface throughflow at the location of a seep that had been previously gauged in the early to mid-1970s [Harr, 1977; Triska *et al.*, 1984]. The trench was constructed by intercepting subsurface water from a natural seepage face using steel sheeting that was anchored into exposed bedrock approximately 5 cm and then sealed with hydraulic cement. Intercepted subsurface water was routed to a calibrated 15° V-notch weir that recorded stage at 10-minute time intervals using a 1-mm resolution capacitance water level recorder (TruTrack, Inc., model WT-HR). Precipitation was measured with a tipping bucket and storage gauge in a small canopy opening on the hillslope. The drainage area of the hillslope was delineated from a total station topographic survey of the entire hillslope (0.17 ha) and verified by a water balance calculation. We used a rounded value of 0.2 ha in all analyses.

Soil water content ( $\theta$ ) dynamics were measured using water content reflectometers (WCR) (CS615, Campbell Scientific, Inc.) installed horizontally (i.e., with the slope) at 3 depths (30, 70, and 100 cm) in 3 soil pits in lower portion of the hillslope

(Figure 4.1). The nests were located 15, 20 and 25 m from the slope base. The WCRs were calibrated using soil cores extracted from several locations at the H.J. Andrews, including WS10 (*Czarnomski et al.*, unpublished data). Tensiometers were collocated with each WCR; however, the tensiometer data proved unreliable, and thus, are not presented in this paper. Transient saturation in the soil profile was measured by 27 wells instrumented with capacitance water level recorders (TruTrack, Inc., model WTDL 8000). Most of the wells were installed to bedrock (i.e., refusal); however, about a quarter of them were installed in the soil profile to depths where *Ranken* [1974] observed sharp saturated hydraulic conductivity contrasts. The capacitance water level recorders were only able to detect water levels  $>7.5$  cm from the bottom of the well. Suction lysimeters were installed in four nests in an upslope transect (Figure 4.1). Each nest contained 30, 70 and 90 cm depths, except site A, where bedrock was  $<90$  cm deep. Water from the lysimeters that accumulated between sampling intervals (from daily to biweekly) was collected over a 3 month period (Nov-Jan).

#### 4.2.2 Tracers

Two line source tracers were applied to the hillslope immediately before a large winter rainstorm (66 mm, 49 h duration) that began on 9 December 2002 at 21:30. 20.9 g of Amino G acid monopotassium salt (AGA), a fluorescent dye [*Smart and Laidlaw*, 1977], and 4.0 kg of bromide (as LiBr solution) were applied 19 and 33 m from the trench, respectively. The AGA was injected ( $\sim 50$  mL of  $1.86 \times 10^4$  mg L<sup>-1</sup> every 10 cm) beneath the organic horizon soil using a syringe over a 2.5 m long application line and Br<sup>-</sup> was sprayed with a backpack sprayer along a 5.0  $\times$  0.10 m application area. Both

tracers were monitored continuously at the trench for the first 9 days of the experiment using a field fluorometer (10-AU, Turner Designs, Inc., Sunnyvale, CA) equipped with a flow-through cell and data logger for AGA and an ion-selective electrode for  $\text{Br}^-$  (TempHion®, Instrumentation Northwest, Inc.). Grab sampling extended the AGA breakthrough for 100 days and it provided additional samples for calibrating the  $\text{Br}^-$  selective electrode ( $N=107$ ,  $r^2 = 0.99$ ). Both tracers were monitored until concentrations during storm events were at background levels (~100 days). Background concentration of  $\text{Br}^-$  was non-detectable ( $<0.45 \text{ mg L}^{-1}$ ) and potential background concentrations of AGA were evaluated during a previous storm event, since dissolved organic carbon can interfere with AGA fluorescence. Maximum background AGA concentrations reached about  $10 \text{ } \mu\text{g L}^{-1}$  during peakflow conditions.

Oxygen-18 ( $^{18}\text{O}$ ) samples were collected weekly at the hillslope trench (01-Nov-01 to 11-Feb-03), WS10 (13-Feb-01 to 4-Feb-03), and as bulk precipitation (01-Jan-00 to 11-Feb-03). Soil water samples from the lysimeters were collected at time intervals between daily and weekly from 2-Oct-02 until 11-Feb-03. Storm samples were collected between 2 and 4 hour intervals from the hillslope and WS10 for several storms during the fall 2002 to winter 2003 period. The samples were analyzed primarily for  $^{18}\text{O}$ ; however, geochemical ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{SiO}_2$ ) analyses were completed for some samples for several storms. Rainfall was sampled sequentially (4.4 mm increments) over this period for  $^{18}\text{O}$  using samplers as described in *Kennedy et al.* [1979].  $^{18}\text{O}$  samples were analyzed at the USGS Stable Isotope Laboratory in Menlo Park, California using an automated version of the  $\text{CO}_2\text{--H}_2\text{O}$  equilibration technique of Epstein and Mayeda [1953]. The  $\delta^{18}\text{O}$  values are reported in per mil (‰) relative to a standard as

$\delta^{18}\text{O} = (R_x/R_s - 1) \times 1000$ , where  $R_x$  and  $R_s$  are the  $^{18}\text{O}/^{16}\text{O}$  ratios for the sample and standard (VSMOW), respectively. The analytical precision ( $\sigma$ ) was 0.11‰ based on submitted blind duplicate samples.

#### 4.2.3 Modeling

Hydrograph separation and residence time models were used to quantify the proportions event and pre-event water and to estimate residence times of various runoff components within the hillslope and catchment. The TRANSEP (transfer function-hydrograph separation) model was used to estimate the event water contributions and residence time distributions [Weiler *et al.*, 2003]. TRANSEP embraces the temporal event water signal and does not assume that rainfall travel times instantaneously reach the stream (or hillslope trench) [Chanat and Hornberger, 2003]. In conventional hydrograph separation models (approach 1), bulk rainfall composition is used as the event water component, which can influence the separation during the early portion of an event by rain that has not yet fallen [e.g., see McDonnell *et al.*, 1990; Pionke *et al.*, 1993]. Instead, TRANSEP lags event water contributions according to an assumed residence time distribution (RTD) and thus more realistically represents the nature of event water contributions [Joerin *et al.*, 2002; Laudon *et al.*, 2002; Renshaw *et al.*, 2003; Chanat and Hornberger, 2003; Weiler *et al.*, 2003]. In this study, we used two different RTDs: a two parallel linear reservoir model and a gamma model depending on which model best-fit the  $\delta^{18}\text{O}$  data and had identifiable parameters (see Weiler *et al.* [2003] for additional details regarding the model).

We examined the residence time of soil water in several positions on the slope, hillslope runoff, and stream baseflow using a lumped parameter time series model to interpret observed  $\delta^{18}\text{O}$  variations [Maloszewski *et al.*, 1983; Stewart and McDonnell, 1991]. The residence time models predict output  $\delta^{18}\text{O}$  (i.e., soil water, seepage, or stream flow) as a weighted sum of the past  $\delta^{18}\text{O}$  input composition. The weighting function or residence time distribution (RTD) describes the time it takes water to travel from the ground surface to an outflow location (soil water, seepage, or stream flow). The RTD that gives the best fit between observed and simulated output  $\delta^{18}\text{O}$  is assumed to represent the flow system [McGuire and McDonnell, submitted]. The transfer of approximately three months of daily  $\delta^{18}\text{O}$  inputs into the soil was described using a RTD representing a one-dimensional solution to the advection-dispersion equation under volumetrically sampled conditions for a semi-infinite medium [Kreft and Zuber, 1978; Stewart and McDonnell, 1991]. The residence time model for WS10 is discussed elsewhere [McGuire *et al.*, submitted]; however, it generally follows the same approach as the soil water residence time models, expect that an exponential distribution was used for the RTD. The hillslope residence time was estimated using the same method as WS10.

## 4.3 Results

### 4.3.1 Threshold Runoff Response

A series of 18 storms were monitored during the wet-up phase of the 2002/2003 winter rainy season (Table 4.1, Figure 4.2). Storm events were defined as periods of major rainfall separated by at least 24 h of rainfall intensities averaging less than 0.1 mm  $\text{h}^{-1}$ . Gross precipitation amounts ranged from 13 to 230 mm with 30-minute maximum



intensities of  $9 \text{ mm h}^{-1}$ . During the early part of this period, several fall storm events caused small responses in both hillslope and WS10 runoff (storms 1 to 3). The storm runoff for WS10 could be explained entirely by channel interception of storm rainfall (i.e., based on measurements of bank-full width at 10 m intervals,  $767 \text{ m}^2$ ). However, the hillslope response indicated that some small portion of the hillslopes contributed to stormflow even though soil moisture response was negligible. One exception to this was a  $<2 \text{ mm}$  rain burst on 27 October (Figure 4.2), where only WS10 responded to channel interception inputs.

Hillslope seepage was sustained throughout the dry fall period and constituted about 15% of the total discharge at the WS10 outlet (i.e., from 1 Sept. to 1 Nov.). Hillslope contribution to WS10 total discharge dropped dramatically after a major storm on 7 November to an average contribution of approximately 2% of WS10 for the remainder of the study. The transition period, beginning with storm event 4, signified the initial soil moisture response on the hillslope (Figure 4.2) and the first event with a measurable stormflow or quickflow ( $Q_f$ ) volume (i.e., as defined by *Hewlett and Hibbert* [1967]). The hillslope  $Q_f$  was 3.5 mm and WS10  $Q_f$  was 5.3 mm. Quickflow ratios ( $Q_f/P$ , i.e.,  $Q_f/\text{gross precipitation}$ ) generally increased through time after this event (Figure 4.3a) with total storm precipitation explaining most of the temporal variance. Stormflow was not produced at either the trench or catchment for rainfall amounts less than 30 mm. Antecedent precipitation, as the 14-day cumulative precipitation prior to a storm ( $AP_{14}$ ), did not appear to influence significantly the observed near linear relationship between rainfall amount and hillslope stormflow volume that occurs after the 30 mm threshold (Figure 4.3b). The exception to this was when the  $AP_{14}$  was less than

20 mm, and then the values plotted below the overall trend (Figure 4.3b). Otherwise,  $Q_f/P$  ratios for WS10 exceeded 30% when total storm precipitation was greater than about 65 mm. Other AP indices (e.g., 7 or 30 day) did not describe the nature of rainfall- $Q_f/P$  relationship any better than  $AP_{14}$ .

Some insight into the threshold hillslope processes can be obtained through analysis of temporal soil moisture dynamics ( $\theta$ ) within the hillslope. Soil moisture at 30 cm responded relatively quickly to rainfall, reflecting a primarily vertical infiltration wetting front. There were no apparent differences in response times of shallow  $\theta$  measurements between the three slope locations. In contrast,  $\theta$  at each 100 cm location exhibited marked time lags compared trench outflow and were correlated to hillslope  $Q_f/P$  ratios ( $r = -0.66$  to  $-0.70$ ,  $p$  value  $< 0.04$ ).

The first storm with an observable  $\theta$  response at 100 cm was event 5, which responded 1 to 19 h after the peak of hillslope throughflow (Figure 4.2). However, the soil moisture sensor located at the upper 100 cm site showed no response to this event, while the mid-position 100 cm site lagged the seepage response more than the lower site. Storm 6, which occurred on 9 December, increased WS10 baseflow by more than an order of magnitude and shifted  $\theta$  to levels that were maintained throughout the rest of the winter period (wet phase, Figure 4.2). Thereafter, soil moisture responses at all sites were nearly synchronized with the hillslope peak runoff. Soil moisture responses generally peaked prior to the hillslope peak runoff by approximately 5 h. This indicated that hillslope water contributed from distances at least represented by the position of these sensors ( $> 25$  m). The general order of soil moisture response for each hillslope position began with the lower site and became more delayed for each upslope site, which

suggested that the hillslope wet-up from the bottom. While saturation was not directly observed using the soil moisture sensors at any time during this study (i.e.,  $\theta$  did not plateau), observed values of  $\theta$  at 100 cm between storms 8 and 11 indicated soils were near-saturated. Soil moisture content at the lowest site was generally higher compared to the upper upslope positions.

During the winter period when antecedent wetness was high, soil moisture at 100 cm lagged rainfall intensities (defined as the time of mass center) on average by 0.3, 0.3, and 0.5 h for the lower, mid, and upper water content reflectometers (WCRs), respectively, indicating a rapid moisture response in the lower soil profile. Estimated vertical fluxes for the two upper WCRs exceed saturated hydraulic conductivity by approximately a factor 10 (average soil profile  $K_{sat} \approx 45 \text{ cm h}^{-1}$ ).

No saturated zones were detected in any wells over the study period. While our observations were limited by the number of wells we deployed (27) and the water level recorder detection limit (7.5 cm), it is striking that transient water tables were not observed. Saturated soils (<5 cm) were periodically observed at the bedrock-soil interface in wells located above the seep and in other near-stream areas that were used to sample water during storms.

#### 4.3.2 Hillslope-Catchment Hysteresis

Stormflow from the hillslope and WS10 with measurable  $Q/P$  ratios were examined in sequence (commencing after the 3 month summer dry period, Figure 4.2) to understand the timing of hillslope contribution and hillslope-catchment coupling through the wet-up period. Figure 4.4 shows the temporal dynamics of hillslope and catchment

coupling during our study period. During the first event with a measurable quickflow ratio (storm 4), the hillslope and catchment were synchronized through the entire 3-day storm event, which had low  $Q_f/P$  ratios of 2 and 3% for the hillslope and WS10, respectively. Four days later, another storm occurred, approximately doubling the  $Q_f/P$  ratios, during which the hillslope discharge led the WS10 hydrograph revealing a hysteretic relationship between the two runoff responses. This effect became more pronounced during storm 6 when the  $Q_f/P$  ratios were 10 and 15% for the hillslope and WS10, respectively.

The hillslope and WS10 were completely synchronized and contributed equal unit area discharge to the storm hydrograph throughout storm 8 (Figure 4.4). Interestingly, during storm 9, the hysteresis pattern reversed. This occurred when the  $Q_f/P$  ratio was at the highest observed value for the hillslope and again doubled the  $Q_f/P$  ratio of the previous storm event (see Table 4.1). Also during this period, the time lag between peak soil moisture response and hillslope discharge was greatest (soil moisture responses peaked 5 to 10 h prior to the discharge peak). The  $Q_f/P$  ratio for WS10 decreased slightly for the next storm (storm 10) to 36% and the hillslope-WS10 discharge pattern remained anti-clockwise. As the  $Q_f/P$  ratio decreased back to values similar to storm 8, the relationship began to approach the clockwise hysteresis pattern again (storm 11). Comparison between the hillslope and WS10 was not possible after storm 11, since the hillslope runoff gauge failed after that storm.

### 4.3.3 *The Hillslope Tracer Response*

We then applied tracers to test the degree of connectivity between the hillslope and catchment as suggested by the hydrometrics and determine potential mode of transport (matrix or preferential flow) in hillslope soils. Tracers were applied prior to a major rainfall event that began on 9 December 2002 at 21:30 (defines the start of the experiment,  $t=0$ ). Tracer breakthrough was extremely rapid and almost identical for both tracers even though  $\text{Br}^-$  was applied 14 m farther upslope than AGA (Figure 4.5). Tracer concentrations peaked 40.4 and 40.3 h after the start of rainfall, for AGA and  $\text{Br}^-$ , while the time of mid-rise on the breakthrough curve was 37.3 and 38.4 h for AGA and  $\text{Br}^-$ , respectively. Peak soil moisture from the two lower slope positions and peak hillslope throughflow all occurred 38.8 from  $t=0$ , while peak soil moisture from the upper site coincided with the peak breakthrough concentrations (40.2 h). This suggests that a more continuous hydrologic connection of near-saturated soils occurred on the lower 25 m of hillslope at  $\sim 40$  h during this storm. These response times indicate subsurface flow velocities were between 0.47 to 0.51  $\text{m h}^{-1}$  and 0.82 to 0.86  $\text{m h}^{-1}$  for the AGA and  $\text{Br}^-$ , respectively.

During the first 10 days of the experiment, both AGA and  $\text{Br}^-$  concentrations were high and responsive to rainfall with smoother  $\text{Br}^-$  concentrations indicating greater dispersion compared to the AGA tracer (Figure 4.5). After this period, the concentrations began to slowly recede. Overall, 19 and 53% of the applied tracer mass was recovered for AGA and  $\text{Br}^-$ . Due to difficulties in quantifying background concentrations [see *Smart and Laidlaw, 1977*], the AGA recovery is uncertain and likely overestimated. Nevertheless, this does not affect the finding of coincident breakthrough, since AGA

concentrations were at least 4 times greater than potential background concentration estimates.

#### 4.3.4 Event Water Contributions

The fraction of event water comprising the hydrograph at peakflow was generally less than 30% (Table 4.2). Based on only two storms, the fraction of event water decreased with larger stormflow contribution (i.e.,  $Q_f/P$ ) for both the hillslope and stream (Table 4.2). The rainfall isotopic composition varied significantly through the storm periods (e.g., Figure 4.6), which led to high uncertainties [Genereux, 1998] using conventional isotope hydrograph separation methods [Sklash, 1990; Buttle, 1994]. For that reason, and to extract more information from the isotope record of these storms, the TRANSEP modeling approach was used. In the example TRANSEP simulation shown in Figure 4.6, it is clear that the hillslope and stream responded differently to the same  $\delta^{18}\text{O}$  rainfall input. The hillslope tracer response was lagged and damped compared to the stream signal. Generally, event water contributions were lower at the hillslope compared to WS10 (Table 4.2). Figure 4.7 shows the event water residence time distributions (RTDs) for two hillslope storms (events 5 and 8) and three WS10 storms (events 4, 5, and 8). These were obtained by a fitting procedure; goodness-of-fit statistics are shown in Table 4.2 along with the estimated mean residence times (MRT) of event water. Estimated MRTs ranged from 8 to 34 h. Hillslope event water contribution was lagged considerably compared to WS10 for storm 5 (Figures 4.6 & 4.7), even though both sites contained roughly the same amount of event water (19 and 27% for hillslope and WS10 mean event water contribution, respectively).

The three storms shown in Figure 4.7 for WS10 indicate that the event water RTDs shifted through time toward more dispersed event water contributions as antecedent moisture conditions increased. The rapid event water response in the first event in Figure 4.7 (storm 4) likely represented direct channel interception of rainfall only, since the  $Q/P$  ratio was so low. Direct precipitation on saturated areas remained constant in WS10, since lower hillslope soils never became saturated and stream channel expansion was severely confined to the predominantly bedrock channel. In storm 5, the event water RTD for WS10 (and the hillslope) was delayed. This appeared to correspond to a lag in soil moisture and a hysteretic hillslope contribution that led the WS10 hydrograph (Figure 4.4) during relatively dry conditions. When antecedent moisture increased (storm 8), event water response was almost immediate, indicating hydrologically connected hillslope conditions. The large  $Q/P$  ratio for event 8 precluded a solely channel interception mechanism for delivering event water to the stream. Several of the RTD tails approach the length of the storms, suggesting that event water contributions continue for longer periods than we show in Figure 4.7.

#### 4.3.5 *Soil Water, Hillslope Runoff, and Streamflow Residence Time*

The time lags estimated by the event water RTDs describe <30% of the overall contribution to runoff. Thus, the origin of the pre-event water fraction, which dominates the hydrograph during wet and dry conditions, is of greater interest for understanding how hillslopes are linked to their catchments. Figure 4.8 illustrates an example dataset and simulation for one of the suction lysimeters (D70). The marked rainfall and soil water  $^{18}\text{O}$  depletion that occurred during mid-December (Figure 4.8) allowed for high

modeling efficiencies (Table 4.3). The soil water MRTs are conservatively high estimates, since the time associated with each sample was the end of the collection period, which would tend to attenuate the  $\delta^{18}\text{O}$  signal of preferential flow that may have been collected in the lysimeters. The RTDs for each lysimeter are shown in Figure 4.9. Estimated mean residence times for shallow soils (30 cm) were approximately 13 days, while deeper soils (70 and 90 cm) were 22 days. Shallow lysimeters exhibited greater dispersion compared to the deep lysimeters (Figure 4.9, Table 4.3) ( $r=-0.73$ ,  $p$  value = 0.011). Mean residence time estimates were also well correlated to soil depth ( $r=0.87$ ,  $p$  value = 0.001), but showed little correlation with upslope distance ( $r=0.45$ ,  $p$  value = 0.177). The estimated MRTs are slightly less than turnover times calculated from a water balance. Total rainfall over the lysimeter collection period (~90 days) was about 900 mm and the average water content for the upper meter of soil was about 33% (storage  $\approx$  300 mm). Therefore, assuming steady-state conditions, the turnover time for 90 cm of soil would be approximately 30 days ( $90 \text{ days} / [900 \text{ mm} / 300 \text{ mm}] = 30 \text{ d}$ ). MRTs determined from the isotope analysis seem reasonable, but indicate some contribution of more rapid pathways than the simple piston-flow water balance estimate might suggest. Both estimates imply that more than 2 pore volumes were replaced within the soil over our study period and suggest that most of the soil water is mobile.

Stream and hillslope water residence times were significantly longer than soil water MRTs. MRTs estimated for WS10 and the hillslope were 1.2 and 1.8 years, respectively (Table 4.3). Exponential RTDs were assumed to represent the spatial integration of flow paths at the catchment and hillslope scales. These values were determined from models representing non-storm conditions and thus, largely reflect



baseflow. Residence times estimated for WS10 and other basins in the HJA showed no correlation to catchment area, but were strongly correlated to median flow path length and gradient determined from topographic analyses, indicating the importance of hillslope contributing areas (for detailed discussion of these data, see *McGuire et al.* [submitted]). While the estimated MRT for the hillslope was 0.6 years longer than its catchment (WS10), parameter uncertainty (Table 4.3) suggests that the values are indistinguishable, especially considering that about 35% fewer samples were collected from the hillslope compared to WS10 (i.e., hillslope sample collection began later in study).

#### **4.4 Discussion**

##### *4.4.1 Harr 1977 Revisited with New Hydrometric Results*

The study initiated by Harr in the early 1970s has been cited more than 90 times in the literature (Science Citation Index) and is a benchmark paper in hillslope hydrology. *Harr* [1977] focused on the hydrometric characterization of subsurface stormflow in WS10 during wet winter conditions. The major findings from that study that relate to this work are: 1) subsurface saturated areas expanded upslope and generally persisted over the lower 12-15 m of the hillslope, 2) transient saturation occurred at mid- to upslope locations at the soil-saprolite interface (persisted for <20 h), 3) subsurface fluxes in these saturated zones were high (i.e., 10-25 cm h<sup>-1</sup>) in mid- to upslope locations if connected to the more permanently saturated zones at the based of the slope, 4) unsaturated flow dominated over all but the lower 12-15 m of the hillslope with water flux directed more laterally downslope during storms and vertically between storms, and 5) streamflow

responded to rainfall inputs prior to hillslope response. More recent studies on steep hillslopes have also shown the importance of unsaturated flow [McDonnell, 1990; Wilson *et al.*, 1991; Torres *et al.*, 1998], the perching of transient saturated zones at soil-bedrock or saprolite interfaces [Hammermeister *et al.*, 1982; Woods and Rowe, 1996; Freer *et al.*, 2002; Buttle *et al.*, 2004], and the modulation of subsurface water fluxes between vertical and lateral directions between and during storms, respectively [Hoover, 1985; Jackson, 1992].

Even though saturation ( $>7.5$  cm) was not directly measured in our study, it was periodically observed during wet conditions (Figure 4.2) in non-recording wells and suggested by the high soil water content measured at 100 cm depth. Maximum saturated thickness observed by Harr [1977] never exceeded 25 cm in the soil profile during similar types of events (unpublished data, maintained by the HJA LTER program and Forest Science Data Bank), indicating thin zones of saturation developed during wet, storm conditions. The location of saturation development occurred over the low hydraulic conductivity saprolite [Ranken, 1974; Harr, 1977].

The initiation of hillslope runoff was not studied by Harr [1977], since field observations were made during only winter conditions. In our study, we measured hillslope runoff from dry to wet conditions and found a threshold rainfall amount necessary initiate hillslope runoff. While rainfall events less than 30 mm certainly generated some streamflow at the WS10 outlet, they did not generate significant subsurface stormflow at the trenched hillslope. Instead events  $<30$  mm that occurred through the fall period, contributed to soil water recharge reducing soil water deficits. Threshold stormflow effects that occur after about 20 mm rainfall have been also

observed in other humid Pacific Rim studies [*McDonnell*, 1990; *Sidle et al.*, 1995; *Tani*, 1997].

The striking hysteresis patterns between hillslope and catchment runoff reveal greater complexity in hillslope-catchment interactions than observed by *Harr* [1977]. *Harr* and other investigators [e.g., *Weyman*, 1970; 1973; *Turton et al.*, 1992; *McGlynn et al.*, 2004] have found that hillslope runoff is often delayed compared to streamflow, suggesting that transient saturated conditions are a necessary precursor to hillslope runoff, where lateral flow contributions cause the peak of hillslope subsurface flow to follow that of the stream. Our results show a more dynamic interaction between hillslope and catchment runoff through a range of antecedent conditions. During the transition phase (Figures 4.2 and 4.4), the hillslope leads the WS10 hydrograph and contributes a greater proportion of flow on the rising limb of the WS10 hydrograph. As antecedent wetness increases, the hysteresis pattern is reversed (Figure 4.4). While some studies have shown that hillslope runoff can peak prior to streamflow [*Peters et al.*, 1995; *Kim et al.*, 2004], no study that we are aware of shows hillslope-streamflow lags that change direction over time. Our ability to detect these nuances is due to the lack of any complicating near-stream features, and the fact that we have been able to record every successive storm through the wet-up and transition from dry summer to wet winter.

These observations are consistent with the hydrogeomorphic model of *Sidle et al.* [2000], where during wet conditions, subsurface flow expands over greater slope distances, preferential flow commences (see discussion below), and moisture thresholds are differentially exceeded in various hillslopes. *Buttle et al.* [2004] and *Tromp-van Meerveld and McDonnell* [in review] demonstrated recently that differential rates of

filling of bedrock depression storage exerts a nonlinear control on hillslope runoff contribution. Their work and our observed 30 mm threshold for hillslope subsurface flow initiation would suggest that the hysteresis loop reversal may be due to differential storage effects from other hillslopes that produce more rapid contribution from other hillslopes compared to the gauged slope. This bedrock depression storage hypothesis, however, is unlikely at WS10 due to the slope steepness, relatively uniform bedrock topography, and high drainable porosity soils.

Another hypothesis is that different subsurface flow processes were invoked once the hillslope attained its wettest state and became hydrologically connected. When the hysteresis pattern was reversed (i.e., storm 9), the  $Q/P$  ratio (41%) reached its maximum observed value in the storm sequence shown in Figure 4.4. This suggests a minimum contribution from lower 46 m of the hillslope if soils were 100% saturated [see *Harr*, 1977]. Since soils were not saturated, upslope contributions must have extended significantly beyond this distance to potentially include the entire slope. Based on *Harr*'s work, it was shown that transient saturation at the soil-saprolite interface can develop in the upper most portions of the hillslope (soil pit 1, Figure 4.1) and that if these zones become connected to saturation at the slope base, lateral subsurface fluxes could increase by 2 to 4 times. Therefore, we hypothesize that during the wettest winter storm conditions, the connection of transient saturated zones at mid- and upslope positions with saturated zones at the slope base is mostly likely responsible for the change in hysteresis direction observed in our study. Even though we cannot rule out the possibility of differential contribution from other hillslopes, soil moisture and applied tracer (see below) responses during storm 6 (an earlier event) supports the connection hypothesis.

#### 4.4.2 *Residence Time as a Dynamic Concept*

The runoff response from WS10 is extremely rapid and appears to be among the highest quickflow ratios reported in the literature [Hewlett and Hibbert, 1967; Harr, 1977; McGlynn *et al.*, 2002]. Yet, stormflow is dominated by pre-event water with an average age exceeding 1 year. These observations are at the core of Kirchner's [2003] old water paradox, where catchments promptly respond to rainfall events, but yield old water. Our results suggest that there are multiple sources of this "old" water, each with their own respective age distribution. For example, soil water residence times in the unsaturated zone were much younger (10-25 d) than baseflow residence time (>1 year), but older than sources activated during storms, which were reflected by the breakthrough of applied tracers and mean event water residence times (<30 h). While, the integration of residence time distributions from each of these sources would likely reveal a similar distribution as introduced by Kirchner *et al.* [2000], where runoff contains short-term responsive behavior and simultaneous long-term persistence or memory to past inputs, the contribution of each component is dynamic.

#### 4.4.3 *A Conceptual Model of Runoff Generation and Residence Time*

A conceptual model that integrates the dynamic residence time results with the physical processes described by the combined hydrometric observations of Harr [1977] and of the current study is synthesized in Figure 4.10. During dry conditions that occur though summer and fall periods, baseflow is sustained by a deep subsurface source with a residence time on the order of 1-2 years. The exact flow pathways of deeper subsurface water are unknown. We suspect that much of the deeper flow occurs through bedrock

fracture exfiltration and within the highly weathered parent material (i.e., saprolite) that reaches depths greater than 4 meters on the upper sections of our experimental hillslope and elsewhere in WS10 and is characterized by low hydraulic conductivity [Ranken, 1974].

Geochemistry samples collected from this hillslope at lowflow were significantly higher in base cation concentrations than samples collected from more than 60 locations elsewhere in the HJA (Sebestyen unpublished data). Bedrock weathering products in WS10 are dominated by calcium and sodium [James, 1978], which were both expressed at higher concentrations preceding and following storms 4 and 5 at the hillslope (Figure 4.11), suggesting that bedrock contributions were diluted through the progression of the storms. The geochemical evidence, combined with sustained lowflow seepage and documented bedrock fracturing [James, 1978; Harr, 1977], suggests a mechanism similar to that which Asano *et al.* [2002] found, namely a bedrock water dominance of hillslope seepage (and potentially lowflow at the WS10 outlet). Other studies in steep forest catchments have also suggested that bedrock contributions are important in generating runoff [Anderson *et al.*, 1997; Onda *et al.*, 2001]. Thus, seepage from bedrock exfiltration in the hillslope maintains a small and thin saturated zone at the bedrock-soil interface in the lower portions of hillslope, which supports perennial seepage at the trench face (Figure 4.10, dry conditions).

As hillslope soil water deficits are gradually reduced from fall rain storms, the contribution from soil water drainage increases. During transitional period storms, only the lower hillslopes contribute to stormflow. This is supported by the small contributing areas (quickflow ratios <10%) of transitional storm events and insignificant or delayed

upper slope soil moisture response. Geochemical dilution that occurred during these transitional storms, suggests that deeper sources become diluted by significant event water contributions (~20%) with residence time distributions that are significantly delayed (i.e., 10-30 h) due to transport through unsaturated soils. This is represented in Figure 4.10b under transitional conditions by the additional event water reservoir with contribution  $\alpha$ . Clearly, the overall age distribution with a mean of 1-2 years is not affected significantly by mixing with 20% event water with an age of 20 h.

As antecedent wetness increases, saturation expands during storms, maintaining a limited thickness (<20 cm), from largely unsaturated and transient-saturated upslope contributions. Significant lateral contributions from saprolite are unlikely since hydraulic conductivities fall off rapidly with depth; thus, contributions from deeper sources ( $\beta$ , Figure 4.10b) diminish as illustrated by the dilution of geochemistry in Figure 4.11. Soil water RTDs show no evidence of downslope aging and indicate a gradual vertical movement of water through upper soils between storms, which effectively “prime” the system with pre-event water that is relatively young compared to bedrock seepage. Soil water can then contribute to runoff through vertical and lateral preferential flow, as evidenced by the  $\text{Br}^-$  tracer experiment, and through the expanding saturated zone development during storms that tends to occur at major hydraulic conductivity contrasts (e.g., saprolite interface). The latter soil water contribution process will likely cause mixing with stored matrix water and subsequently change the composition of lateral flow emulating older water [cf. *McDonnell*, 1990]. This effect would lessen over time as soil pore volumes are flushed multiple times yielding a more constant younger water source. Soil water is represented by the shallow reservoir in Figure 4.10b with a mean residence

time of about 10-25 d, which becomes the dominant contribution to runoff as catchment wetness increases. The shallow processes that develop during storm events with high antecedent wetness are illustrated in Figure 4.10 by an expanded saturated zone at the base of the slope, transient saturation at mid- to upper slope areas, and unsaturated preferential flow. Estimated event water residence time distributions indicated a rapid response from preferential flow processes compared to the residence time distributions during drier conditions, which were delayed due to transport through unsaturated soils (Figure 4.7). This suggests that the residence time of event water contributions vary over time. The breakthrough of applied tracer also indicates that event water contributes from considerable distances, which may occur at the timescale of a storm event.

#### 4.4.4 *Hillslope-Catchment Connections*

Based on the conceptual model presented above, the nature of hillslope and catchment connections evolves through time as shallow processes become activated with increasing wetness and storm size. The importance of hillslope contributions to stream networks is often neglected during lowflow conditions when potential hillslope contributions are masked by the near-stream storage of groundwater. Our results would indicate that hillslope contributions to the stream can be significant as shown by the large volumetric flow contribution of a single hillslope during the dry period (i.e., 15% of the total WS10 discharge). Localized seepage areas, such as this, would not be seen in most catchments due to the presence of near-stream storage zones, which were removed in WS10 by debris flows, exposing hillslope seepage areas. These seepage areas may be important for hyporheic processes [Battin, 1999; Bencala, 2000] and biogeochemical



transformations that occur at the terrestrial-aquatic interface [e.g., *Cirimo and McDonnell*, 1997].

After the catchment wet-up occurred, the hillslope contribution to the stream represented 2% of the total WS10 discharge reflecting the hillslope proportion of the total WS10 catchment area, and thus, a near 1:1 specific discharge relationship. During wet periods, connectivity within the hillslope increases as the saturated zone expands upward from the base of the slope at the soil-saprolite interface. At this interface, soil moisture remains near 84% of saturation [*Ranken*, 1974] and consequently, is more easily converted to saturated conditions compared to shallower soil (30-70 cm), which might be between 50 and 70% of saturation. Soil moisture response at this depth can be extremely rapid, as indicated by the 0.3 to 0.5 h response time of our 100 cm water content reflectometers. Recent studies on hillslopes with similarly high conductivity and porosity soils that largely remain unsaturated, have suggested that rainfall intensities on relatively wet soils can produce pressure waves that cause rapid moisture response in the unsaturated zone [*Torres et al.*, 1998]. While soil moisture lag time estimates calculated from the centroid of rainfall inputs simplifies the convoluted pressure response to the rainfall intensity distribution, it does suggest rapid soil moisture changes occur at depth in the soil profile within the lower portion of the hillslope. The precise mechanism delivering water to this depth remains unclear. A pressure wave translation to depth augmenting soil moisture response cannot be rejected [see *Torres*, 2002]. On the other hand, the rapid  $\text{Br}^-$  breakthrough and the observed coincident soil moisture response suggest advective preferential flow transport is most plausible. Opportunities for solute

transport from remote regions of the catchment seem feasible and increase over the time-course of an event as transient saturated areas connect.

The applied tracer experiment demonstrated the potential connectivity and new water contribution from distant upslope areas to the stream by the rapid tracer breakthrough observed at the slope base. Subsurface flow velocities determined from our tracer experiment were approximately 50 times higher than the pore water velocities (i.e.,  $q/\theta$ ) computed from the highest observed unsaturated fluxes found in *Harr* [1977] (assuming  $\theta \approx 0.45$ ). *Tsuboyama et al.* [1994] and *Sidle et al.* [1995] found similar average pore water velocities ( $0.508 \text{ m h}^{-1}$ ) for plot-scale  $\text{Cl}^-$  additions over a range of antecedent wetness conditions and application rates. *Anderson et al.* [1997] observed rather high velocities ( $3.6 \text{ m h}^{-1}$ ) of  $\text{Br}^-$  that were transported through saturated subsoils and bedrock. However, they did not observe any preferential flow through unsaturated soils and suggested a plug flow mechanism for soil water transport. *Harr* [1977] estimated that saturated zone fluxes directed entirely downslope could be between  $0.1$ - $0.25 \text{ m h}^{-1}$  if mid- to upslope saturated areas along the subsoil contact are continuous and connected. Assuming  $\theta$  is about  $0.55$  for saturated soils, pore water velocities would approximate velocities determined by our tracer breakthrough curves. This suggests that either contiguous saturated conditions existed between the tracer application and the trench and/or that unsaturated preferential flow delivered tracer to the trench. In either case, hydrologic connectivity clearly extends far upslope during wet conditions, even though the extent of this contributing area is unknown. This is particularly striking since our hillslope is unambiguously planar.

#### ***4.5 Concluding Remarks***

We examined the temporal dynamics of hillslope and catchment runoff response using combined hydrometric, isotopic, and applied tracer approaches. Our results show an evolving relationship between hillslope and catchment runoff through a wet-up period, which was largely controlled by moisture thresholds and expansion of saturated areas upslope. While not directly observed in this study, expanding saturated areas within a thin zone above weather bedrock were inferred through soil moisture patterns, applied tracer breakthrough, large quickflow ratios, and previous studies at this site. Event water residence time distributions and rapid breakthrough from an applied upslope tracer addition, demonstrated that contributing areas extend far upslope during events. Despite these rapid transport processes, we found soil water and runoff mean residence times that were greater than the timescale of storm events. Soil water mean residence times exhibited no evidence of downslope aging and were between 10 and 25 days for shallow and deep soil, respectively. On the other hand, runoff from the hillslope and catchment during non-storm conditions was between 1 and 2 years old. These results led to a dynamic conceptual model describing variable physical flow pathways and residence times through changing antecedent wetness conditions that illustrate different stages of hillslope connectivity.

This study demonstrates that temporal hydrometric data alone are not sufficient to develop an understanding of the dynamic connectivity between hillslope and catchment flow pathways. Applied and natural tracers enabled us to characterize the transport timescales of water sources that contribute to runoff generation during and between events that help define clear hillslope-catchment process linkages.

#### 4.6 Acknowledgments

This work was supported through funding from the National Science Foundation (grant DEB 021-8088 to the Long-Term Ecological Research Program at the H. J. Andrews Experimental Forest) and Department of Forest Engineering at Oregon State University. We thank C. Creel, G. Downing, J. Moreau, and S. Sebestyen and B. Morrisette for assistance in the field; D. Henshaw for access to meteorological, streamflow, and R. D. Harr data (HF01) from the FSDB; C. Luce for performing the bromide analysis; R. Hooper and P. Schuster for geochemical analysis; and F. Swanson, J. Jones, and M. Weiler for many useful discussions. We also thank R. D. Harr and D. Ranken for initiating the hillslope studies at WS10.

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Table 4.1. Storm characteristics for events during the fall 2002-winter 2003 wet-up period.

Storm No.	Beginning of Precipitation		Duration [h]	Gross Precipitation <sup>a</sup> [mm]	30-min Maximum Intensity [mm/h]	Antecedent Precipitation [mm]		Quickflow ratio <sup>†</sup> $Q_f/P$	
	Date	Time				14-Day	30-Day	Hillslope	WS10
1	16-Sep-2002	18:10	25	23	4.1	9	0	n.a.	n.a.
2	29-Sep-2002	7:50	44.2	29	5.6	23	0	n.a.	n.a.
3	3-Oct-2002	9:10	15.5	13	3.6	29	52	n.a.	n.a.
4	7-Nov-2002	12:30	107.5	177	7.6	19	19	0.02	0.03
5	16-Nov-2002	10:00	61.8	31	6.1	177	179	0.04	0.07
6	9-Dec-2002	21:30	49.5	66	6.6	33	101	0.10	0.15
7	12-Dec-2002*	14:50	94	96	6.1	85	140	n.a.	n.a.
8	20-Dec-2002	2:30	82.5	60	7.1	168	180	0.23	0.21
9	29-Dec-2002	21:00	88.3	79	5.1	194	310	0.42	0.41
10	2-Jan-2003	5:30	60.2	66	6.6	225	392	0.14	0.36
11	11-Jan-2003	3:20	79.8	51	6.6	186	425	0.23	0.19
12	21-Jan-2003‡	11:00	40.2	23	8.6	51	282	0.03	0.05
13	24-Jan-2003	1:50	83.8	98	6.6	74	304	0.33	0.44
14	29-Jan-2003	7:10	148.3	152	8.6	121	312	0.38	0.56
15	15-Feb-2003	11:00	170	140	5.1	15	282	0.16	0.25
16	5-Mar-2003	2:10	307	230	7.1	81	174	0.40	0.61
17	19-Mar-2003	13:30	100.2	126	4.1	247	352	0.33	0.49
18	24-Mar-2003	20:00	68.8	84	7.6	173	412	0.31	0.47
Mean =								0.22	0.31

<sup>a</sup>Storm events are defined as periods of major rainfall separated by at least 24 h of rainfall intensities averaging < 0.1 mm/h.

\*A complex low rainfall intensity storm and hydrograph occurred during this period.

‡From this date onward, hillslope discharge was predicted from a regression equation using WS10 due to gauge failure.

<sup>†</sup>Quickflow ratios ( $Q_f/P$ ) were determined by projecting a linear  $0.55 \text{ L s}^{-1} \text{ km}^{-2} \text{ h}^{-1}$  slope from the onset of storm runoff [Hewlett and Hibbert, 1967].  $Q_f/P$  is shown as not applicable (n.a.) if the separation was not possible or if  $Q_f/P < \text{calculated channel interception for WS10}$ .

Table 4.2. Isotope hydrograph separation results.

			No. of		Peakflow	Mean	Model	Mean
			Runoff $\delta^{18}\text{O}$	MRT <sup>b</sup>	Event	Event	Efficiency	Absolute
	Storm	Date	Samples	[h]	Water	Water	[-]	Error
					[%]	[%]		[%]
<i>Hillslope</i>								
	Storm 5	16-Nov	Gamma	14	16	20	0.87	0.04
	Storm 8	20-Dec	TPLR	38	20	10	0.40	0.18
<i>WS10</i>								
	Storm 4	7-Nov	TPLR	50	28	11	0.78	0.13
	Storm 5	16-Nov	Gamma	13	8	34	0.90	0.07
	Storm 8	20-Dec	TPLR	40	34	15	0.50	0.16

<sup>a</sup>Event water residence times were estimated using the TRANSEP model [Weiler *et al.* 2003].

<sup>b</sup>Mean residence time (MRT) is calculated numerically from a multi-parameter transfer function.

Table 4.3. Mean residence times (MRT) for soil water and baseflow at the hillslope and catchment scales.

		MRT( $\pm 2\sigma_p$ ) <sup>‡</sup>	$D_p$ ( $\pm 2\sigma_p$ )	Model Efficiency	Mean Absolute Error
	Model	[d, y]	[-]	[-]	[‰]
<i>Soil Water Residence Time</i> [days] <sup>a</sup>					
(Sampler, Depth [cm])					
A30-1	DM	14( $\pm 4.6$ )	0.24( $\pm 0.17$ )	0.85	0.71
A30-1	DM	14( $\pm 6.6$ )	0.29( $\pm 0.31$ )	0.80	0.83
A32	DM	10( $\pm 2.8$ )	0.18( $\pm 0.10$ )	0.86	0.86
A34	DM	12( $\pm 3.0$ )	0.19( $\pm 0.11$ )	0.86	0.81
A70	DM	22( $\pm 3.3$ )	0.08( $\pm 0.07$ )	0.89	0.63
B30	DM	12( $\pm 3.2$ )	0.17( $\pm 0.10$ )	0.83	0.82
B70	DM	24( $\pm 1.8$ )	0.03( $\pm 0.01$ )	0.80	0.88
B95	DM	20( $\pm 2.2$ )	0.08( $\pm 0.04$ )	0.94	0.43
C30 <sup>†</sup>					
D30	DM	16( $\pm 2.2$ )	0.08( $\pm 0.04$ )	0.93	0.46
D70	DM	19( $\pm 3.1$ )	0.14( $\pm 0.07$ )	0.92	0.45
D92	DM	25( $\pm 2.8$ )	0.03( $\pm 0.02$ )	0.72	0.57
<i>Baseflow Residence Time</i> [years] <sup>b</sup>					
Hillslope	EM	1.8( $\pm 0.43$ )		0.67	0.08
WS10	EM	1.2( $\pm 0.29$ )		0.49	0.15

<sup>‡</sup>Approximation of the 95% confidence limit of parameter estimate (mean residence time [MRT] and dispersion [ $D_p$ ]).

<sup>†</sup>No suitable model was found to fit the data.

<sup>a</sup>Based on the approach of *Stewart and McDonnell* [1991].

<sup>b</sup>From *McGuire et al.* [submitted]

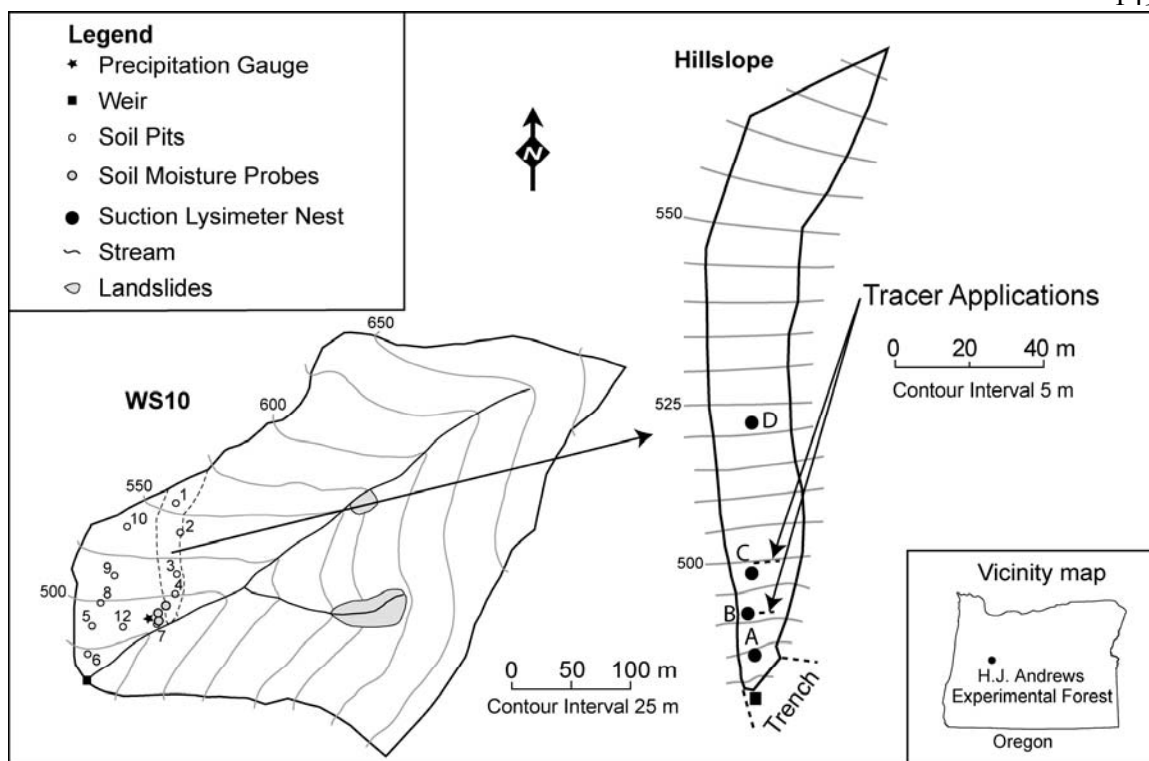


Figure 4.1. Map of WS10 showing the location of instrumentation and hillslope study area.

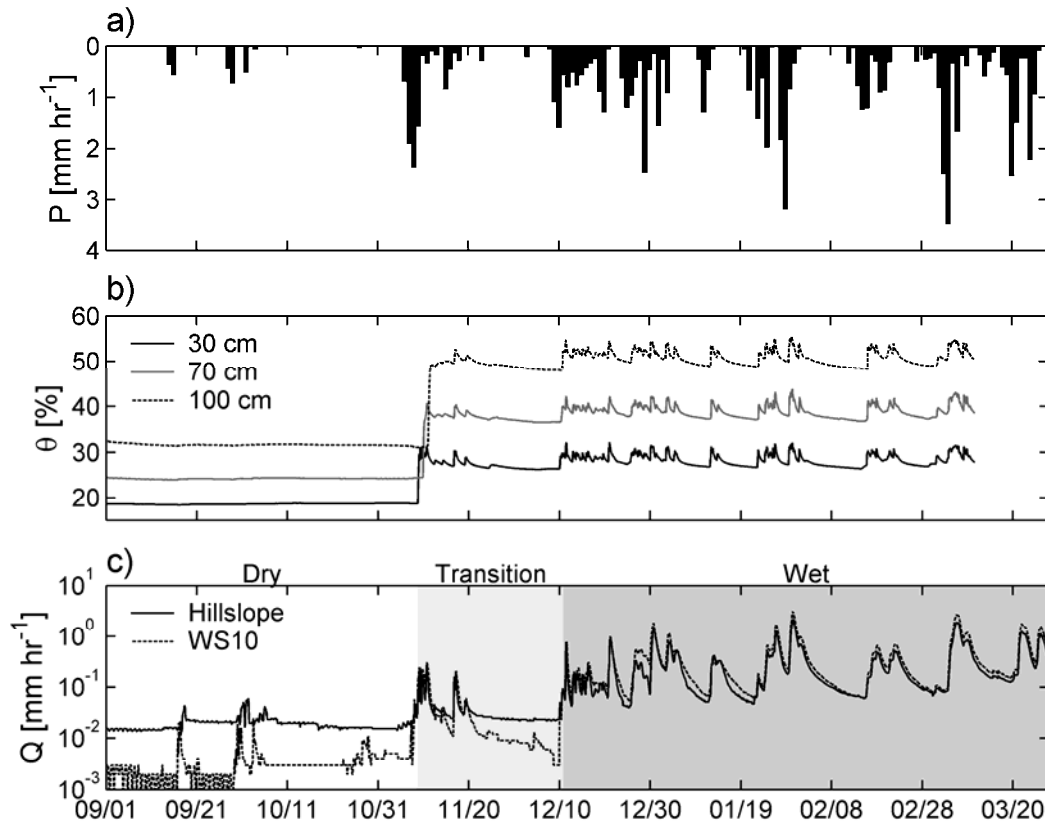


Figure 4.2. Time series of the hydrologic conditions of the study period: (a) precipitation, (b) volumetric water content ( $\theta$ ) from the lower nest of water content reflectometers, and (c) discharge from the hillslope and catchment. The shading indicates the wetting phases during this study period: the dry period is characterized by no soil moisture response, the transition period corresponds to an increase in hillslope soil moisture and stream baseflow, and the wet period represents elevated baseflow conditions and approximate synchronization between hillslope and stream discharge.

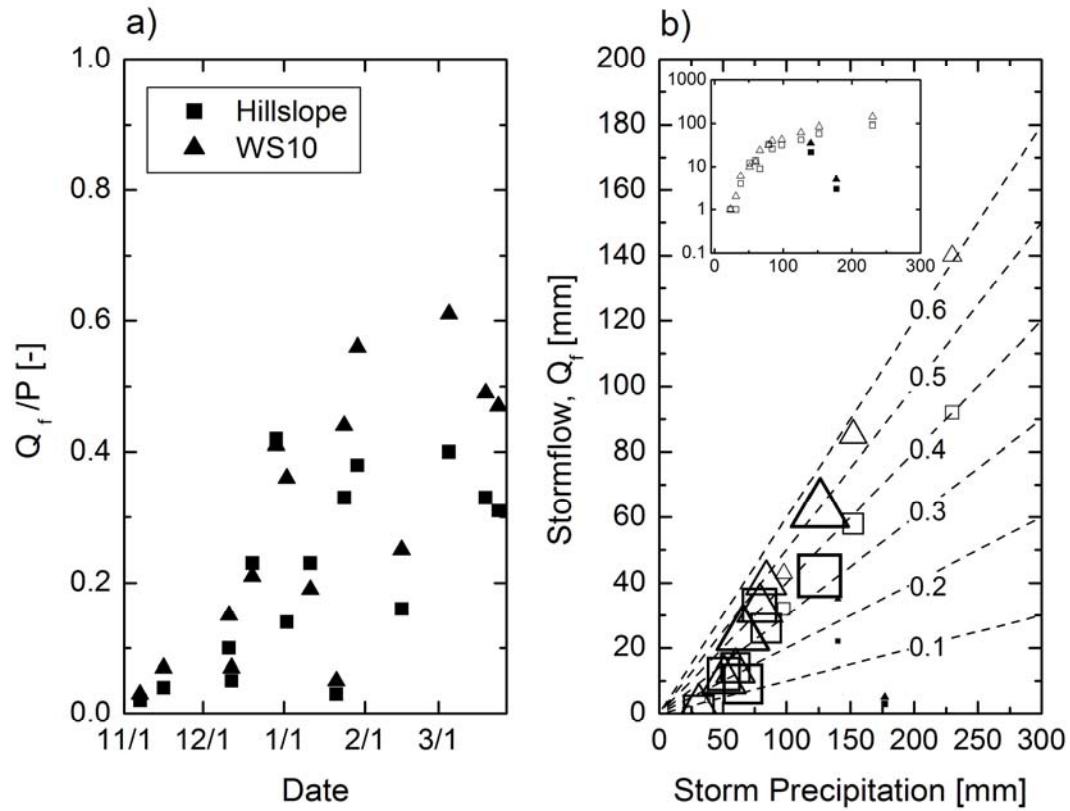


Figure 4.3. (a) Quickflow ratios ( $Q_f/P$ ) over time and (b) total storm precipitation and stormflow [as per *Hewlett and Hibbert, 1967*] relationships for the hillslope (squares) and WS10 (triangles). The size of the symbol indicates relative antecedent precipitation ( $AP_{14}$ ) and filled symbols (right graph) are storms that occurred when  $AP_{14} < 20$  mm. The dashed lines show quickflow ( $Q_f/P$ ) ratios and inset figure expands the y-axis logarithmically.

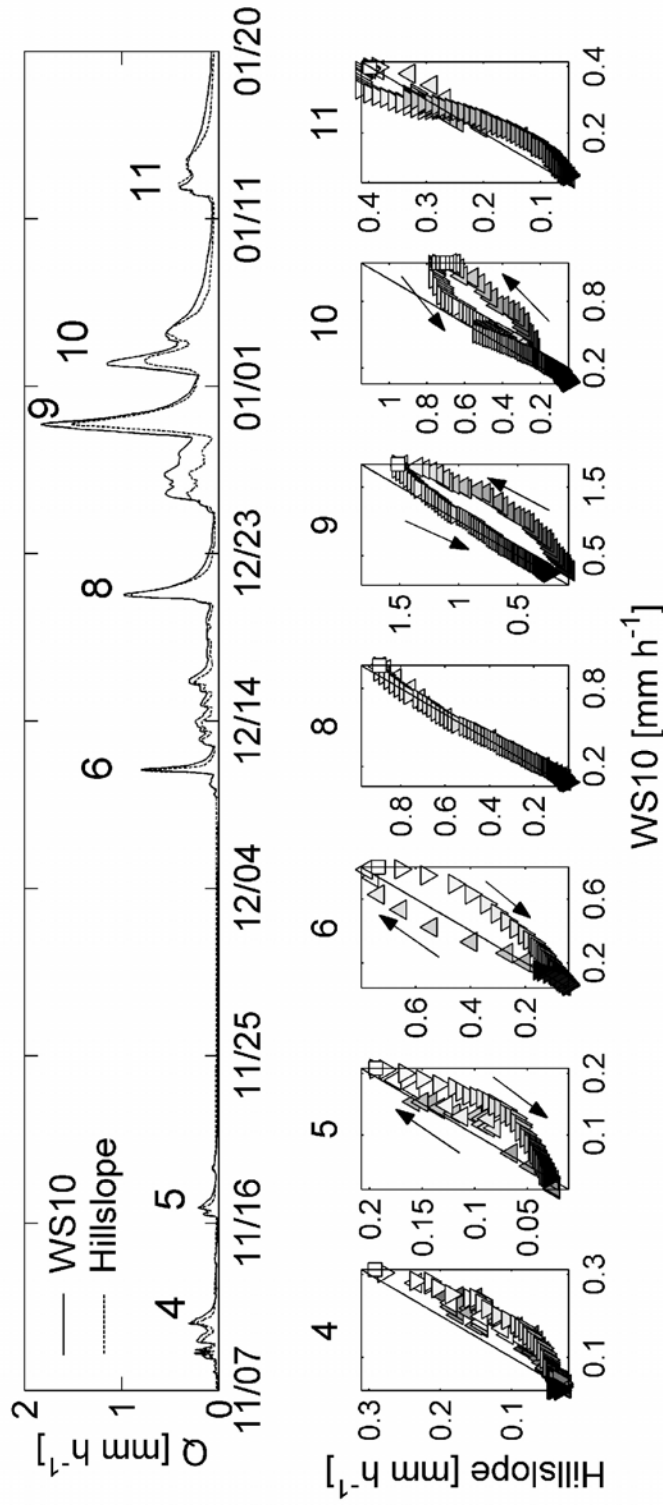


Figure 4.4 Temporal dynamics of hillslope-catchment coupling through the wet-up period. The upper graph shows the time series of the continuous discharge data with enumerated storms that identify the scatter plots in the lower set of graphs. Upward triangles indicate the rising limb of the WS10 hydrograph and downward triangles indicate the falling limb. The grayscale symbol color shows the time sequence to and from the WS10 peakflow (square).

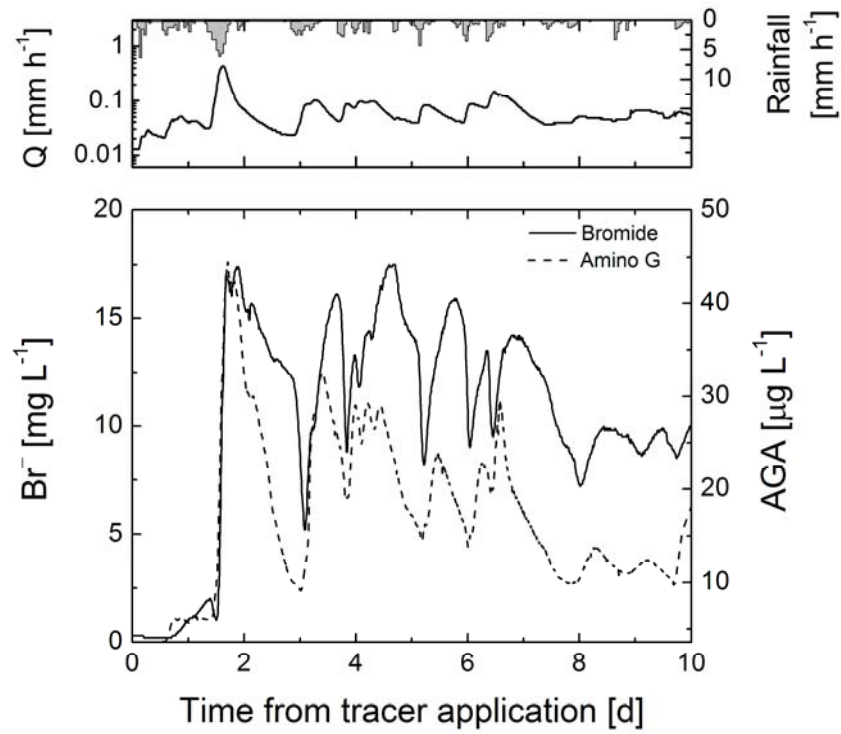


Figure 4.5. Tracer breakthrough curves of bromide ( $\text{Br}^-$ ) and Amino G acid (AGA), which were applied as line-source additions 33 and 19 m, respectively from the hillslope seepage trench (rainfall and hillslope runoff shown in panel).



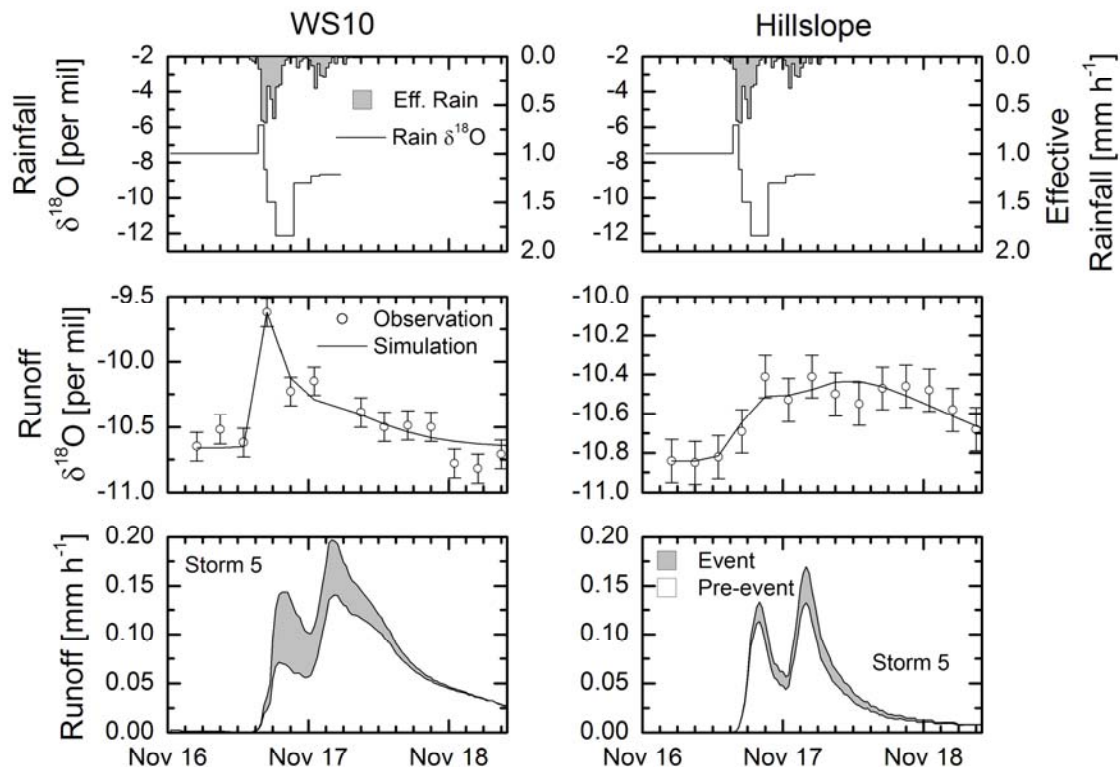


Figure 4.6. TRANSEP isotope hydrograph separations for storm 5 for WS10 (left) and the hillslope (right). The upper plots show rainfall  $\delta^{18}\text{O}$  and effective rainfall amounts that contribute to stormflow [see *Weiler et al.*, 2003] (both sites received the same inputs). The middle plots depict the observed and simulated  $\delta^{18}\text{O}$  for WS10 (left) and hillslope (right). The errorbars represent  $\delta^{18}\text{O}$  analytical precision (0.11‰). The bottom plots show the hydrograph separations by the shaded region in the (event water runoff).

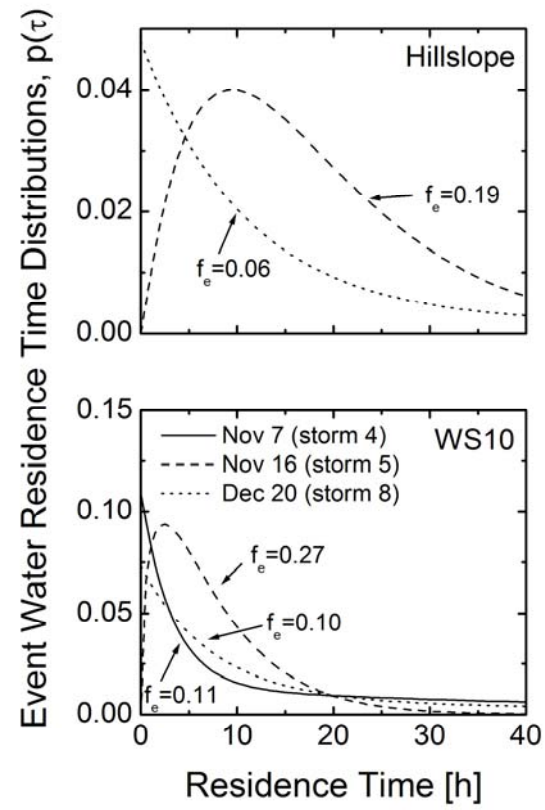


Figure 4.7. Event water residence time distributions for storms 4, 5, and 8. Mean event water contributions ( $f_e$ ) for each storm are included.

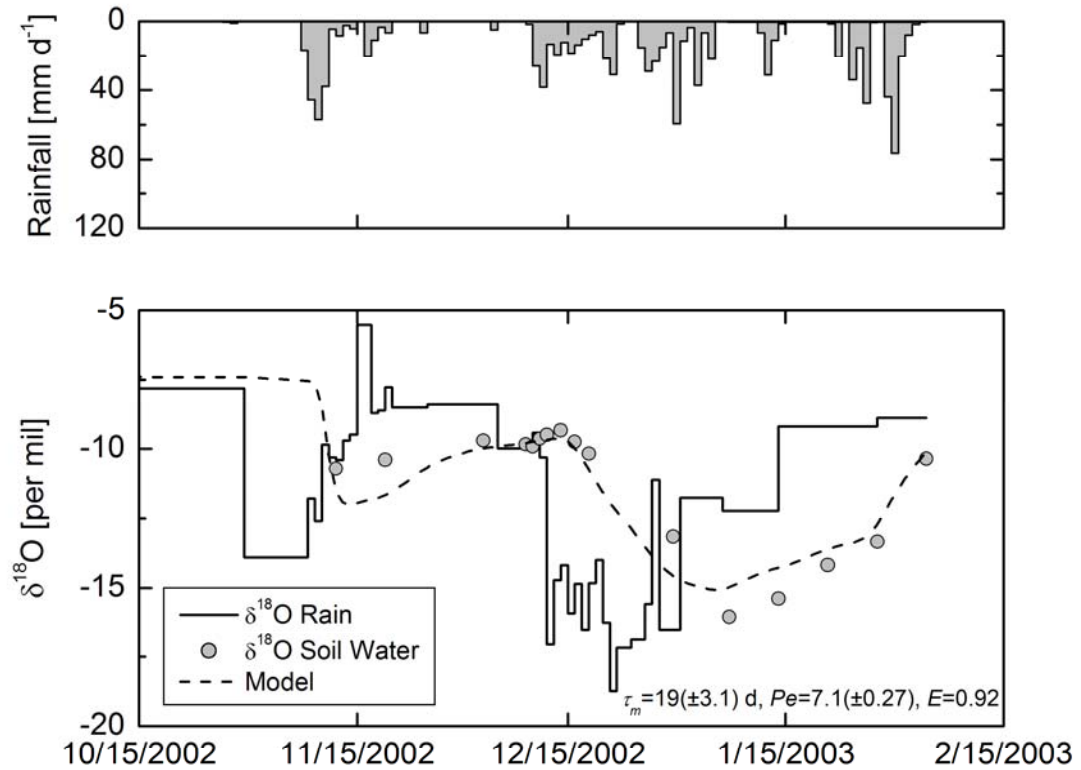


Figure 4.8. An example  $\delta^{18}\text{O}$  simulation for lysimeter D70 modeled using a one-dimensional advection-dispersion model. The mean residence time ( $\tau_m$ ) for this simulation is 19 ( $\pm 3.1$ ) days with a Peclet number ( $1/D_p$ ) of 7.1 ( $\pm 0.27$ ) (i.e., a fitting parameter describing ratio of advective to dispersive timescales).

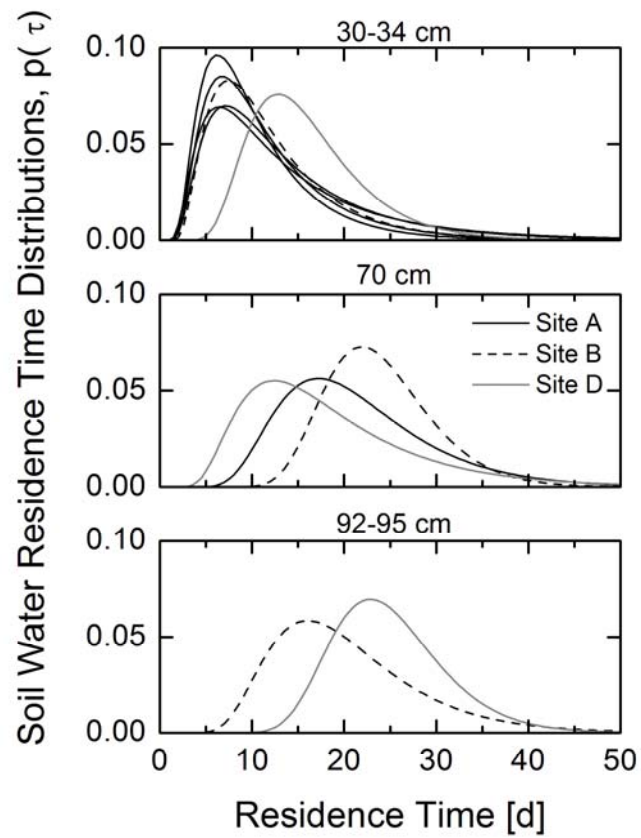


Figure 4.9. Soil water residence time distributions for sites A (lower slope), B (middle slope), and D (upper slope) for three different soil depths 30, 70, and 90 cm. Additional details are given in Table 4.3.

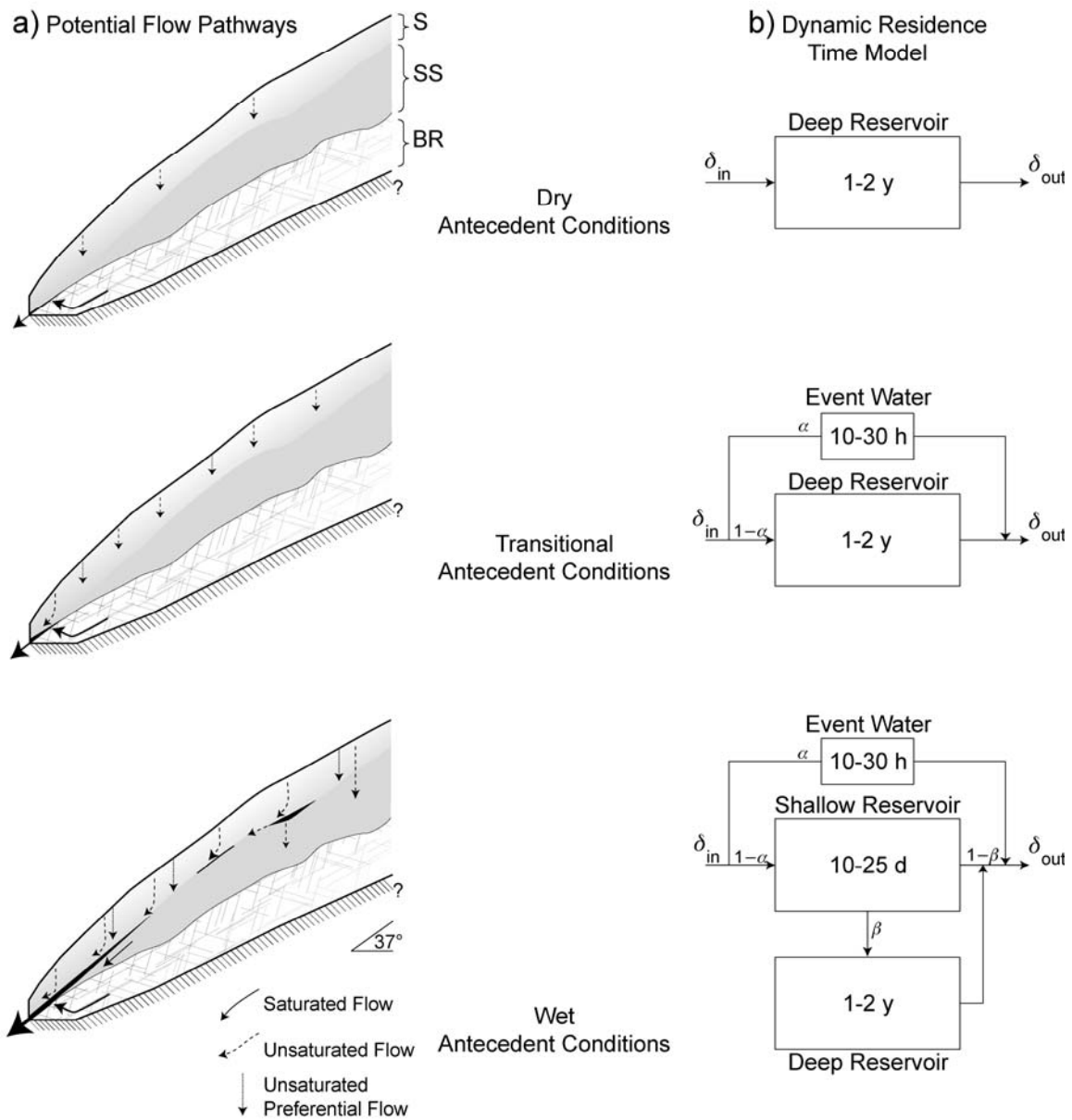


Figure 4.10. A diagram of a conceptual model illustrating the variable flow pathways (a) and residence times (b) contributing to runoff through three wetness phases. The hillslope is represented by a soil layer, a subsoil layer (weathered bedrock), and bedrock and shows hypothesized flow pathways during three different antecedent wetness stages. Residence time components change under different wetness conditions and are illustrated by the conceptual reservoirs denoted with mean residence times.  $\delta_{in}$  and  $\delta_{out}$  designate tracer input and output signals and the parameters  $\alpha$  and  $\beta$  indicate the proportions of event water and deep subsurface water, respectively. Note: not drawn to scale.

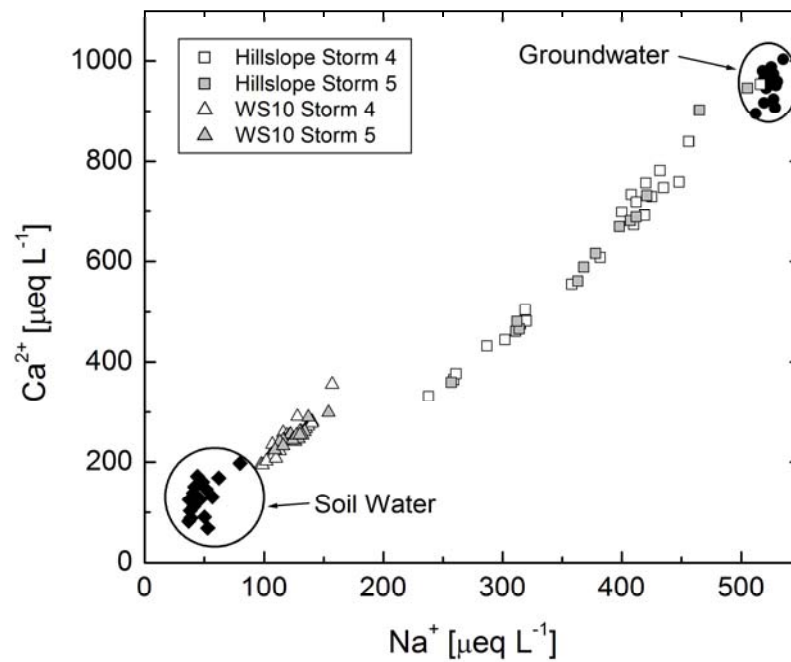


Figure 4.11. Calcium and sodium mixing diagram for storms 4 and 5. Groundwater samples were collected from summer/fall lowflow hillslope seepage, while soil water samples were collected from the suction lysimeter nests over through the Nov.-Dec. wetting period. Stream samples are shown from the time of hydrograph rise until recession flows reached pre-event levels. Soil water concentrations were approximately equivalent values reported in *Sollins et al.* [1980], which were collected on the same slope.

## **5 Integrating tracer experiments with modeling to infer water residence times**

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## 5.1 Introduction

Field studies in hillslope hydrology often reveal complex hydrological processes that operate across a range of spatial and temporal scales and antecedent wetness conditions [Dunne, 1978; Anderson and Burt, 1990; Bonell, 1993; Blöschl and Sivapalan, 1995]. These complex hydrological descriptions that we develop from the field studies are difficult to incorporate within a modeling framework due to the disparity between the scale of measurements and the scale of model sub-units and the natural heterogeneity of catchments [Beven, 2001; Blöschl, 2001]. Thus, many hydrologists have moved away from fully distributed physically-based models and toward more conceptually-based models that describe dominant hydrological processes at the hillslope and catchment scales [Bergström, 1991; Blöschl, 2001]. However, parameters represented in many conceptual models are often not physical or related to physical properties, and therefore cannot be established prior to a model calibration-validation exercise. An additional problem is that the information content in a rainfall-runoff record limits the complexity of conceptual model structures available to test and explore internal process dynamics [Jakeman and Hornberger, 1993; Kuczera and Mroczkowski, 1998; Seibert and McDonnell, 2002].

Recent model calibration approaches have constrained parameterizations using additional data sources such as tracers [Uhlenbrook and Leibundgut, 2002], groundwater levels and estimated saturation areas [Freer *et al.*, 2004; Franks *et al.*, 1998], and other multiple measures [Mroczkowski *et al.*, 1997; Güntner *et al.*, 1999]. Multi-criteria calibration approaches often result in less adequate, but acceptable fits to observed runoff data (compared to calibration using runoff alone) that are generally more consistent with



process findings [e.g., *Seibert and McDonnell*, 2002]. These models, which focus on internal process dynamics and less on calibration-based schemes, are necessary in reducing predictive uncertainty and to develop new model descriptions that match the level of process understanding and available data information content [*Sivapalan et al.*, 2003]. This is particularly important as interest in catchment water quality increases [*Cirimo and McDonnell*, 1997; *Burns et al.*, 1998; *McDonnell and Tanaka*, 2001], since water sources, stores, and pathways within hillslopes and catchments must be adequately represented in model structures to predict and understand the behavior of solutes (e.g., geochemical, contaminants, or conservative tracer). Increasingly, catchment modelers are challenged to incorporate water quality aspects into models to deal with problems such as acidification [*Stoddard et al.*, 1999], cumulative effects [*Sidle and Hornbeck*, 1991], nutrient cycling [*Creed and Band*, 1998], and total maximum daily loads and contamination. The age, or residence time of water offers a link to water quality, since the contact time in the subsurface largely controls stream chemical composition, revealing information about the storage, flow pathways and source of water in a single measure.

The residence time distribution represents the integrated hillslope or catchment scale response of the diverse flow pathways that participate in solute transport, thus connecting process complexity with model simplification. Water residence times are determined typically by black-box modeling of environmental tracers (e.g.,  $^{18}\text{O}$ ,  $^2\text{H}$ ,  $^3\text{H}$ , CFCs, and  $\text{SF}_6$ ), in which input (rainfall) and output (discharge) tracer concentrations are used to estimate parameters of an assumed time-invariant distribution that represents the residence time [*Maloszewski and Zuber*, 1996; *Turner and Barnes*, 1998; *Cook and*

*Herczeg*, 2000]. With this approach, however, we are unable to directly characterize the shape of the residence time distribution (RTD) and examine the assumption of time-invariance, which are undoubtedly important in controlling the fate and transport of solutes at the hillslope and catchment scales under natural rainfall conditions. While there has been some recent work on deriving residence time distributions from a theoretical perspective based on stochastic-mechanistic models [*Simic and Destouni*, 1999; *Lindgren et al.*, 2004], there has been little experimental work to directly determine the distribution of residence times (with the exceptions of *Nyström* [1985] and *Rodhe et al.* [1996] from roof-covered catchment studies), especially during non-steady-state conditions.

Monitoring applied tracers through storm and non-storm periods offers an alternative approach to black-box modeling, where tracer breakthrough curves can be measured to infer residence time distributions in a more experimental fashion. There have been numerous applied tracer studies on hillslopes [e.g., *Luxmoore et al.*, 1990; *Hornberger et al.*, 1990; *Tsuboyama et al.*, 1994; *Brammer*, 1996; *Buchter et al.*, 1997; *Nyberg et al.*, 1999; *Peters and Ratcliffe*, 1998]; however, most of these studies did not focus on determining hillslope-scale residence time distributions and interpretative models were largely solute transport models (i.e., convection-dispersion models) as opposed to coupled hydrologic-tracer models.

The coupling of solute tracer and hydrologic models allows for a comprehensive evaluation of model structure, in terms of predicting runoff and tracer, and verification that the model is working for the right reasons and is consistent with our understanding of reality [*Klemeš*, 1986; *Wagener*, 2003]. There are very few catchment models that

incorporate tracers in a spatially-explicit manner with limited complexity. For example, HSPF, a commonly used and highly parameterized hydrologic simulation model that is coupled with water quality models, is difficult to calibrate due to the number of parameters and their non-uniqueness [*Doherty and Johnston, 2003*]. Thus, there is a critical need to simplify process complexity to achieve parsimonious models that transcend spatial scales and represent dominant physical processes [*Sivapalan, 2003*].

In this study, we combine the merits of a hillslope scale applied tracer experiment and a simple, spatially-explicit hydrologic model to: 1) identify the dominant processes necessary to explain both water and solute flux, 2) test the simple, parsimonious model constrained by soil hydrologic, runoff, and applied tracer data, and 3) use the model as an exploratory tool to directly infer potential hillslope residence time distributions under steady and non-steady conditions. Our work builds upon the study of *Weiler and McDonnell* [2004a] that introduced a model for performing “virtual experiments” at the hillslope-scale for the purposes of exploring first-order controls on hydrological processes in a controlled environment. Here we apply the same model to a field tracer experiment in an effort to simplify observed process complexity and then use the model to investigate dominant processes controls on water residence time.

## **5.2 Site Description**

The study was conducted in Watershed-10 (WS10, 10.2 ha), which is part of a larger research effort at the H.J. Andrews Experimental Forest (HJA) Long-Term Ecological Research (LTER) program in the west-central Cascade Mountains of Oregon,

USA (44.2° N, 122.25° W) (Figure 5.1). The HJA has a temperate maritime climate with wet mild winters and cool dry summers. The annual precipitation averages 2220 mm, about 80% of which falls between October and April during long duration, low to moderate intensity frontal storms. Relatively light snow accumulations are common, but seldom persist longer than 1-2 weeks and generally melt within 1-2 days. No major snow accumulation was observed during this study (9 December 2002 to 31 March 2003). On average, 56% (28 to 76%) of the annual precipitation becomes runoff. The vegetation is dominated by a naturally regenerated second growth Douglas-fir (*Pseudotsuga menziesii*) stand resulting from a 1975 clear-cut harvest.

The hillslope study area is located on the south aspect of WS10, 91 m upstream from the stream gauging station (Figure 5.1). The 125 m long stream-to-ridge slope is slightly convex with an average gradient of 37°, ranging from 27° near the ridge to 48° adjacent to the stream. Elevation ranges from 480 to 565 m. The hillslope is underlain by bedrock of volcanic origin, including andesitic and dacitic tuff and coarse breccia [Swanson and James, 1975]. Soils, formed either in residual parent material or in colluvium originating from these deposits, are classified as Typic Dystrochrepts [USDA-NRCS, 1999; Sollins *et al.*, 1981]. Soil textures range from gravelly, silty clay loam to very gravelly clay loam. Surface soils are well aggregated, but lower depths (70-110 cm) exhibit more massive blocky structure with less aggregation than surface soils [Harr, 1977]. Beneath the weakly developed A and B horizons is relatively low permeability, partially weathered parent material (saprolite) ranging in thickness from 1 to 7 meters [Ranken, 1974; Sollins *et al.*, 1981]. The depth to unweathered bedrock ranges from 0.4 to 0.6 m at the stream-hillslope interface and increases gradually toward the ridge to

approximately 3 to 8 m. *Harr and Ranken* [1972] had excavated eleven soil pits on the study slope (Figure 5.1) and collected at least six undisturbed soil cores from 10, 30, 70, 110, 130, and 150 cm (200 and 250 cm cores were collected where feasible), totaling 452 soil cores. The samples were analyzed for hydrologic properties including hydraulic conductivity, porosity, pore-size distribution, moisture characteristics, and stone content [Ranken, 1974; Harr, 1977]. Mean values of the six replicated cores were reported in archived data records (Forest Service Data Bank, maintained by the HJA LTER program).

Relatively well defined seeps have been identified flowing from the base of the hillslope soils into the stream channel [Harr, 1977; Triska *et al.*, 1984]. These seeps are highly localized zones of saturated soil related to the microtopography of the unweathered bedrock near the stream or to the presence of vertical, andesitic dikes approximately 5 meters wide, which are located within the southern aspect hillslope [Swanson and James, 1975; Harr, 1977]. The main rationale for selecting this study slope was the richness of local data resources from these previous studies [Ranken, 1974; Harr, 1977; Sollins *et al.*, 1981; Sollins and McCorison, 1981; Triska *et al.*, 1984].

### **5.3 Field Methods and Results**

#### **5.3.1 Field Methods**

A 10 m long trench was constructed to measure subsurface flow at a natural seepage face using steel sheeting that was anchored into exposed bedrock approximately 5 cm and then sealed with hydraulic cement to intercept subsurface water. Intercepted subsurface water was routed to a calibrated 15° V-notch weir that recorded stage at 10-

minute time intervals using a 1-mm resolution capacitance water-level recorder (TruTrack, Inc., model WT-HR). Precipitation was measured with a tipping bucket and storage gauge in a small canopy opening on the hillslope. The drainage area of the hillslope was delineated topographically from a total station survey of the entire hillslope (0.17 ha) and verified by a water balance calculation. We used a rounded value of 0.2 ha in all analyses. A detailed knocking pole survey [Yoshinaga and Ohnuki, 1995] of the lower 30 m of hillslope was used to determine bedrock topography (*Van Verseveld*, unpublished data) and extend soil depth data collected by *Harr and Ranken* [1972].

Two line source tracers were applied to the hillslope immediately before a large winter rainstorm (66 mm, 49.5 h duration) that began on 9 December 2002 at 21:30 h. 20.9 g of Amino G acid monopotassium salt (AGA), a fluorescent dye [*Smart and Laidlaw*, 1977], and 4.0 kg of bromide (as LiBr solution) were applied 19 and 33 m (slope distance) from the trench, respectively. AGA is preferred over other fluorescent dyes since it has lower adsorptive loss in soils [*Trudgill*, 1987]. The AGA was injected using syringes beneath the organic horizon soil over a 2.5 m long application line and Br<sup>-</sup> was sprayed onto the soil surface with a backpack sprayer along a 5.0×0.10 m application area. The AGA concentrations were measured at 2-minute intervals for 9 days using a field fluorometer equipped with a flow-through cell, data logger, and long wavelength oil optical kit (Turner Designs, Inc., Sunnyvale, CA, model 10-AU). Bromide was also measured *in situ* using an ion-selective electrode (TempHion®, Instrumentation Northwest, Inc., accuracy = ± 5%) and recorded on a Campbell CR10X (Campbell Scientific, Inc.) data logger at 5-minute time intervals until 31 March 2003. Grab samples were collected from the start of the experiment until 18 February 2003 at both

the trench (AGA: 272 samples, Br: 107 samples) and at the WS10 catchment outlet (AGA: 257 samples, Br: 270 samples). The AGA grab samples were analyzed in the laboratory using the same fluorometer, whereas Br<sup>-</sup> samples were filtered and analyzed using an ion chromatograph at the Boise Aquatic Sciences Lab (Rocky Mountain Research Station, Boise, ID). Background concentrations of AGA were evaluated at the hillslope during a storm prior to the tracer experiment. Maximum background AGA concentrations, which coincided with discharge peaks, ranged from 3 to 10 µg L<sup>-1</sup>. Background Br<sup>-</sup> concentrations were not detectable (<0.45 mg L<sup>-1</sup>).

### 5.3.2 *Field Results: Tracer Breakthrough*

The response to the tracer application was extremely rapid (Figure 5.2). Tracer concentrations peaked 40.4 and 40.3 h after the start of the storm (9 Dec. 2002 21:30 h), for AGA and Br<sup>-</sup>, respectively. These response times indicate that subsurface flow velocities were 0.47 m h<sup>-1</sup> and 0.82 m h<sup>-1</sup> for the AGA and Br<sup>-</sup>, respectively. The near synchronous response of both tracers suggests strong lateral preferential flow and little difference in transport between the two application distances. During the first 10 days of the experiment, both AGA and Br<sup>-</sup> concentrations were high and responsive to rainfall with somewhat smoother Br<sup>-</sup> concentrations indicating higher dispersion compared to the AGA tracer (Figure 5.2b inset). After this period, the concentrations began to slowly recede and recovery rates decreased. Overall, 19 and 53% of the applied tracer mass was recovered for AGA and Br<sup>-</sup> at the trench site, respectively. No detectable concentrations of either tracer were observed at the WS10 flume, mainly due to dilution from the higher

discharge in the stream (~2 orders of magnitude volumetric flow). We expected higher recovery rates of AGA, since it was applied much closer to the hillslope trench; however, the low AGA recovery was likely an artifact of sorption to organic material. Also, due to difficulties in quantifying background concentrations [see *Smart and Laidlaw*, 1977], the AGA recovery is uncertain and likely overestimated. Hence, we did not model the AGA breakthrough data.

## **5.4 Modeling Methods and Results**

### **5.4.1 Modeling Methods**

We used a simple physically-based hillslope model, Hill-Vi, to describe water and solute flux at our hillslope natural rainfall conditions during the tracer experiment. This model was based on concepts presented in *Seibert and McDonnell* [2002] and *Seibert et al.* [2003] and was introduced by *Weiler and McDonnell* [2004a] as a tool to perform virtual experiments on hillslopes to address process controls on the generation of subsurface flow. Hill-Vi has been used in subsequent work to test nutrient flushing hypotheses [*Weiler and McDonnell*, in review] and to explore the effects of pre-event water variability on estimated runoff components and the connectivity of hillslope preferential flow networks [*Weiler et al.*, 2003]. This is the first study to use Hill-Vi in conjunction with a field experiment. We based the model structure on our best process understanding determined from WS10 past field investigations [*Harr and Ranken*, 1972; *Ranken*, 1974; *Harr*, 1977]. We present only a brief overview of the model here, highlighting specific features that relate to runoff generation in WS10. Detailed descriptions of the overall model are provided by *Weiler and McDonnell* [2004a].



Hill-Vi is a spatially explicit model that is data driven and solves basic continuity equations within coupled unsaturated and saturated zones. The unsaturated-saturated zone coupling was implemented to represent unsaturated zone conversion to transient saturation during storm events, which is observed frequently in field studies [Harr, 1977; McDonnell, 1990; Bazemore *et al.*, 1994; Montgomery *et al.*, 1997]. The unsaturated zone is defined by the depth from the soil surface to the water table and is characterized by time-variable water content [Seibert *et al.*, 2003]. The saturated zone is defined over an impermeable bedrock surface by the thickness of the water table and the porosity,  $n$ . Lateral subsurface flow is calculated using the Dupuit-Forchheimer assumption and routed downslope using the approach of *Wigmosta and Lettenmaier* [1999], but according to the water table gradients between grid cells. Lateral subsurface flow only occurs within the saturated zone.

Hill-Vi uses a depth function for drainable porosity as a control on transient water table development [Weiler and McDonnell, 2004a]. The drainable porosity is defined by the difference in volumetric water content between 0 and 100 cm of water potential (i.e., approximately from saturation to field capacity). Field observations show that the drainable porosity declines dramatically with depth due to changes in the soil structure and macropore development (Figure 5.3a). Figure 5.3a shows the drainable porosity calculated from soil core data collected at WS10 and an exponential function and prediction limits (95%) that indicate the overall trend and variability in drainable porosity

with depth. The drainable porosity,  $n_d$ , is represented in the model by the following function:

$$n_d(z) = n_0 \exp\left(-\frac{z}{b}\right) \quad (1)$$

where  $n_0$  is the drainable porosity at the soil surface and  $b$  is a decay coefficient.

We calculate the water balance of the unsaturated zone by the rainfall input, vertical recharge into the saturated zone, and change in water content. Recharge from the unsaturated zone to the saturated zone is controlled by a power law relation of relative saturation within the unsaturated zone and the saturated hydraulic conductivity ( $K_{sat}$ ) at the depth of the water table,  $z(t)$  :

$$R(t) = \left(\frac{\theta(t)}{\theta_s}\right)^c k_0 \exp\left(-\frac{z(t)}{f}\right) \quad (2)$$

where  $R$  is recharge to the saturated zone,  $\theta/\theta_s$  describes the relative water content,  $c$  is the power coefficient reflecting a nonlinear response to increased wetness,  $z$  describes the location of the water table surface,  $k_0$  is the surface  $K_{sat}$ , and  $f$  is the hydraulic conductivity shape factor for an exponential  $K_{sat}$  function. Figure 5.3b shows the exponential reduction and considerable variability in  $K_{sat}$  determined from the WS10 data [Ranken, 1974]. Equation 2 represents the vertical water flux component described by Harr [1977], which is essentially based on the Brook and Corey [1964] method. The water balance of the saturated zone is defined by the recharge input from the unsaturated zone, the lateral inflow and outflow, and the corresponding change of water table depth.

Actual evapotranspiration,  $E_{act}$ , is simply estimated based on the relative water content in the unsaturated zone ( $\theta/\theta_s$ ) and the potential evapotranspiration,  $E_{pot}$  [Bergström and Forsman, 1973; Seibert and McDonnell, 2002]:

$$E_{act}(t) = E_{pot} \left( \frac{\theta(t)}{\theta_s} \right) \quad (3)$$

Potential evapotranspiration was assumed a constant value in this study equal to the mean  $E_{pot}$  estimated with a temperature index model [Hargreaves, 1975] ( $1 \text{ mm d}^{-1}$ ), since climatic and moisture conditions remain relatively constant through the winter period at the HJA. Rainfall interception loss was calculated using empirical relationships developed for the HJA [Rothacher, 1963], even though forest canopy characteristics were likely dissimilar. Keim *et al.* [2004] showed that storm-to-storm variability in interception exceeds any differences in stand structure, age, and tree size; thus, Rothacher's regression model provides a first-order approximation for any interception loss.

Solute flux in recharge,  $m_r$ , depends on the average concentration in the unsaturated zone and is determined by:

$$m_r(t) = R(t) \frac{M_{un}(t)}{S_{un}(t) n_{eff}} \quad (4)$$

where  $R(t)$  is the recharge of a grid cell at time  $t$  and  $S_{un}$  is the water storage in the unsaturated zone, and  $n_{eff}$  is the effective porosity (total porosity  $\times$  effective porosity coefficient). Effective porosity is a common simplification describing the porosity available for fluid flow and thus, the available pore space for solute mass transfer [Bear, 1972; Stephens *et al.*, 1998]. The lateral subsurface solute flux is calculated in a similar

fashion by multiplying the subsurface flow with the average concentration in the saturated zone. Mass exchange between the saturated and unsaturated zone under transient water table conditions is contingent on the change in water table depth ( $\Delta w$ ) and the difference between  $n_{eff}$  and  $n_d$  (i.e., the proportion of water that is drained by the falling water table). *Weiler and McDonnell* [2004a] showed that under a falling water table, solute is transferred ( $\Delta m$ ) from the saturated to the unsaturated zone depending on the change in water table position,  $\Delta w$ , and the average concentration in the saturated zone:

$$\Delta m(t) = \frac{M_{sat}(t)}{w(t)n_{eff}} \Delta w(t) (n - \overline{n_d}) \quad (5)$$

$$\overline{n_d} = n_0 b \left[ \exp\left(-\frac{w(t) + \Delta w(t)}{b}\right) - \exp\left(-\frac{w(t)}{b}\right) \right] \quad (6)$$

where  $M_{sat}$  is the actual mass of solute in the saturated zone,  $\overline{n_d}$  is average drainable porosity between the water table,  $w(t)$ , at time  $t$  and  $\Delta w(t)$ , which is the change in water table depth from the previous time step. If the water table is rising, the mass transfer depends on the average concentration in the unsaturated zone [see *Weiler and McDonnell*, 2004a]:

$$\Delta m(t) = \frac{M_{unsat}(t)}{[D - w(t)]n_{eff}} \Delta w(t) (n - \overline{n_d}) \quad (7)$$

where  $D$  is the soil depth and  $M_{unsat}$  is the actual mass of solute in the unsaturated zone. We assume that the rising water table can only mobilize solute within the newly saturated portion of the soil profile. The concentrations in the saturated and unsaturated

zone are calculated under the assumption of complete mixing in each zone and each grid cell.

We found during early model runs that too much tracer had been retained in unsaturated zone, which was an artifact of our well-mixed unsaturated zone assumption. Thus, a bypass term was introduced that allowed for wetness dependent bypass of the unsaturated zone, a process that has been frequently observed in aggregated soils [Radulovich *et al.*, 1992] and in other hillslope studies [e.g., McDonnell, 1990; Leaney *et al.*, 1993; Buttle and McDonald, 2002]. Bypass flow,  $q_{bp}$ , is dependent on the precipitation rate and soil moisture:

$$q_{bp}(t) = P \left( \frac{\theta(t)}{\theta_s} \right)^\beta \quad (8)$$

where  $P$  is the precipitation rate and  $\beta$  is the bypass power coefficient. The mass flux of bypass flow is also assumed as the average concentration in the unsaturated zone similar to Eqn. 4.

The model domain was established using a DEM (4×4 m) constructed from the topographic and soil depth survey. Measured soil hydrologic properties were used to parameterize the model; however, as illustrated by Figure 5.2, there was large variability in the measured data values. Therefore, a Monte Carlo search was performed over expected parameter ranges based on the field data (e.g., Figure 5.2). The objective criteria used to assess model performance were the Nash-Sutcliffe efficiency ( $E$ ) [Nash and Sutcliffe, 1970] for runoff and mass flux. Due to model computation time (30 minutes per model run), a detailed uncertainty analysis [e.g., Beven and Binley, 1992] was not performed; however, we include relative uncertainty measures and scattergrams

of Monte Carlo parameter sets (1000 runs) and Nash-Sutcliffe efficiencies. We defined uncertainty based on the top 20% performing parameter sets as the range between parameter values of the 0.1 and 0.9 percentiles divided by the median parameter value expressed as a percentage, consistent with the approach of *Seibert and McDonnell* [2002]. Therefore, lower uncertainty values indicate a well-conditioned parameter value.

After a calibrated model was achieved (i.e., using field data and inverse methods), we assumed that it provides a first-order approximation for hillslope subsurface flow and transport, and is sufficient for performing numerical experiments (i.e., scenarios) to examine hillslope-scale residence time distributions. Residence time, which describes the time for tracer to travel through the hillslope, can be directly simulated by applying tracer instantaneously to the entire hillslope:

$$RTD(t) = \frac{C_I(t)}{\int_0^{\infty} C_I(t) dt} = C_I Q / M \quad (9)$$

where  $RTD(t)$  is the residence time distribution from the model,  $C_I(t)$  is the concentration of instantaneously applied tracer at  $t=0$  and  $M$  is the tracer mass applied to the entire surface of the hillslope. Thus, the boundary conditions of our model change so that tracer is distributed uniformly over the entire model domain. Since many theoretical residence time distributions are derived for steady-state systems [e.g., *Eriksson*, 1971; *Maloszewski and Zuber*, 1982], we first simulated a steady-state case by running the model with a constant rainfall rate (i.e., average of the study period). Then, we simulated the dynamic case under natural rainfall conditions where we produced different RTD realizations by injecting tracer at monthly intervals from 1 November (immediately after driest three months) to 1 March (the middle of the wet season). All tracers were applied

in the model on the first of the month and were simulated for one year (roughly the time of 100% mass recovery).

#### 5.4.2 Modeling Results: the Line-Source Tracer Experiment

Model calibration for the line-source tracer experiment was based equally on two criteria: 1) how well simulated runoff fit the observed hillslope runoff (runoff efficiency) and 2) how well the simulated mass flux fit observed bromide mass flux (mass flux efficiency). The best parameter set identified in the Monte Carlo analysis (i.e., the average of the two efficiency measures) was also the best parameter set based on only the mass flux  $E$ . The parameters for this model are shown in Table 5.1 along with the best parameter set based on the runoff  $E$ . The identifiability of the parameters is illustrated by the scattergrams in Figures 5.4 and 5.5 and by the relative uncertainty values listed in Table 5.1. Only a few of the parameters appeared to be identifiable (i.e., converge toward a maxima) based on the  $E$  criterion for runoff alone ( $n$ ,  $b$ ,  $c$ , and  $\beta$ ) (Figure 5.4). When the model was calibrated based on the mass flux  $E$ , several parameters resulted in different optimum values ( $n$ ,  $f$ ,  $k_0$ , and  $c$ ). Even though, the efficiency was lower for mass flux, most of the parameters were more identifiable and had lower relative uncertainties (Figure 5.5, Table 5.1). Also, the additional mass flux objective criterion, increased parameter identifiability from calibration determined based on only runoff for  $b$ ,  $n_0$ ,  $f$ , and  $k_0$ . Most calibrated values fell within the range obtained from measured soil hydrologic properties (Table 5.1). For instance, parameters defining the drainable porosity and  $K_{sat}$  depth functions were well within the range of the prediction limits

shown in Figure 5.2. The exceptions were the total porosity calibrated to the runoff data and shape factor,  $f$ , calibrated to the mass flux data.

Figure 5.6 shows the model simulations and observed data timeseries. The best parameter set fit to mass flux had efficiencies of 0.84 and 0.59, while the best parameter set fit to runoff had efficiencies of 0.92 and 0.19 for runoff and mass flux, respectively (Table 5.1). Although, both models produced reasonable simulations compared to runoff, our objective was to simulate both runoff and tracer. Using tracer mass flux as an additional objective criterion we were able reject the best runoff parameter set, since it fit the mass flux poorly (Figure 5.6b). Runoff efficiencies were between 0.76 and 0.88 for parameter sets that produced mass flux  $E > 0.50$ . Mass recovery for both models deviate from the observed recovery; however, the best runoff parameter set significantly underpredicts mass flux during the first 2 weeks of the experiment, when about half of the total recovery occurred. These recovery rates were based on the local mass recovery at hillslope grid cells that represented the trench face. Mass recovery for the entire model domain was 99% for both parameter sets, suggesting that only half of the tracer was recovered due to possible effects of flow around the trench controlled by the bedrock topography.

#### 5.4.3 *Using the Model to Explore the Residence Time Distribution*

Using the best parameter set from above, we simulated a constant rainfall rate of  $0.2 \text{ mm h}^{-1}$  for 416 days (10000 h) to calculate steady-state residence time distributions (RTDs). Once steady-state conditions were reached (83 days after rainfall initiation), we applied an instantaneous conservative tracer to the entire surface of the model domain.



The resulting tracer breakthrough curve normalized according to Eqn. 9 is shown in Figure 5.7. The mean residence time for the model simulation was 92 days. This RTD describes the average transport behavior produced by the model. The simulated distribution is generally exponential (Figure 5.7), but contains a distribution mode at 10 days. We tested the fit of common residence time distributions (e.g., the dispersion and gamma models), but they did not fit the simulated distribution better than the exponential distribution [see *Maloszewski and Zuber, 1996*]. The small mode of the RTD indicates a lack of short flow pathways; nevertheless, it largely reflects the response of a well-mixed reservoir where the outflow decreases monotonically due to mass loss and the lack of new tracer inputs.

The simulation of non-steady RTDs was carried out under a natural rainfall series and by applying separate conservative tracers to the model domain at different times of the year to examine the effect of antecedent wetness on the shape of the RTD. These results are shown in Figure 5.8. Mean residence time varied between 54 and 69 days reflecting more rapid flushing compared to the steady-state case. Cumulative forms of the RTDs are shown in Figure 5.8a, since each individual RTD simulation is easier to distinguish in this form. The driest month, November, had the slowest mass recovery (55 d to recovery 50% mass) and wettest month had the most rapid mass recovery (23 d to recovery 50% mass) (Figure 5.8b). Recovery rates were most significantly influenced by rainfall in the 30-day subsequent period after tracer application. The correlation between mass recovery rates for 25 and 50% recovery and the 30-day subsequent total rainfall were both 0.81, indicating that RTDs were more responsive during wet periods.

The non-steady RTDs diverged from the simple exponential distribution that was fit to the mean residence time of all RTDs shown in Figure 5.8. During the early time portion of the RTDs (i.e., residence times <100 d), most RTDs showed much more responsive behavior and weight at early time (the exception being the November RTD). Thus, the RTDs during wetter months recovered tracer much faster than the exponential distribution, which resulted in less mass recovered during later periods by the simulated RTDs (i.e., residence times >150 d). This effect was largely controlled by the dry summer period (residence times between 150 and 260 d for most RTDs shown in Figure 5.8), when subsurface flow velocities were significantly reduced. Interestingly, the general shape of RTDs reflects the exponential distribution perhaps deviating some during early and late-time periods. The late-time period highlighted in the inset of Figure 5.8b shows that tracer recovery for the March RTD resumed when the system wetted up after the summer drought period. This produced a slightly more linear tail on the logarithmic axes (non-exponential behavior).

## **5.5 Discussion**

### **5.5.1 Model Process Representation**

The twofold model calibration approach with runoff and the applied tracer experiment permitted the exploration of model complexity and process representation designated by our model. Runoff data alone did not contain enough information to represent the hydrological processes determined from field studies at this site, since many model parameters were not well-identified. The inclusion of the line-source tracer experiment and the additional calibration to mass flux, improved parameter

identifiability, which provided further insight to the process controls on hillslope-scale water and solute flux. The measured  $K_{sat}$  values represented by the exponential depth function appeared to be too low for simulating tracer transport, especially deeper in the soil profile. This can be illustrated by examining the better performing values of  $f$  in Figure 5.5 that approach the upper limit prescribed by the data indicating that better performance was achieved for higher  $K_{sat}$  values at depth. Also, effective porosity was quite important for simulating tracer mass flux, which suggests that an immobile soil fraction that controls the mixing volume is an important process to represent in the model structure. The bypass term did not appear to be as significant as we expected based on our field observations, which included dye staining experiments at a nearby site [e.g., see *Weiler and McDonnell*, 2004b], and the observations presented in other published studies [*Trudgill and Coles*, 1988; *Hornberger et al.*, 1990; *Jardine et al.*, 1990; *Radulovich et al.*, 1992]. Optimized bypass parameters fit to both runoff and mass flux showed that smaller values (i.e., less bypass) produced better simulations. However, bypass was necessary to capture the general responsiveness of the tracer and water flux observed at the trench face.

The spatially explicit nature of this model and the inclusion of drainable porosity were ultimately important in representing the location of the trench outflow and the tracer movement across the slope yielding recovery rates approximately equal to our observations. *Weiler and McDonnell* [2004a] demonstrated that when drainable porosity was high (e.g., WS10 soils), modeled water tables were restricted in thickness, tracer mass exchange between the unsaturated and saturated zone was limited, and tracer movement was more affected by bedrock topography. In our study, these factors were

important in modeling the rapid breakthrough of tracer and convergence of tracer along the bedrock surface towards trench face that resulted in similar modeled mass recovery compared to the data.

### 5.5.2 *Model Inferred Residence Time Distributions*

The direct simulation of residence time distributions (RTDs) provided insight to our model representation of flow pathways and an experimental approach to estimating the RTD of a hillslope. The observed tracer breakthrough curves suggested that extremely rapid contribution from upslope areas can occur within the timescale of a single storm event. Surprisingly, the RTDs did not show as rapid of a response. Both the steady and non-steady-state RTD simulations indicated that peak tracer mass flux was delayed. This varied to some extent for the individual non-steady RTDs, since the tracer response was largely controlled by the timing of storm events. However, as illustrated by the steady-state RTD, when soil water deficits were no longer important, the main response occurred about 10 days after the modeled tracer injection. This delay was likely an effect of mixing in the unsaturated domain of the model, which was intended to reflect the slower vertical transport through unsaturated matrix soils. A similar shaped RTD was derived experimentally in the covered catchment study by *Rodhe et al.* [1996]. They found a peak tracer mass flux with a 7 day (flow-time) residence time, which was equivalent to 5.8 mm of flow [see *Rodhe et al.*, 1996], while the equivalent amount of flow for our 10 d peak was about 48 mm. As suggested by *Rodhe et al.* [1996], the existence of the maximum may not be significant, and thus akin to their results, the steady-state RTD in our study approximates an exponential distribution. *Simic and*

*Destouni* [1999] derived the RTD produced in *Rodhe et al.* [1996] with little calibration using a stochastic-mechanistic model. Their theoretical model described nonuniform flow conditions resulting from groundwater recharge through the unsaturated zone, but also incorporated preferential flow, diffusional mass transfer between mobile and relatively immobile water, and random heterogeneity resulting from spatially variable transmissivity. While our model did not explicitly account for all of these processes, the non-steady RTDs reflect variable recharge, preferential flow, and mass transfer between mobile/immobile domains (i.e., saturated/unsaturated zone), suggesting that hillslope RTDs are evidently time-variant.

Under steady-state conditions, the unsaturated and saturated zones become effectively decoupled in our model, since water table fluctuations no longer rise and fall nor remobilize tracer in the unsaturated zone. This process was necessary to encapsulate the dynamic behavior that was illustrated in the observed breakthrough curve and hence the true, unknown RTD. Even though the exponential distribution seemed to describe the predominant trend of the non-steady RTDs (Figure 5.8), simplifying assumptions regarding the subsurface volume and mixing behavior in our model likely resulted in inaccurate late-time RTD behavior. For instance, the shapes of the RTD tails shown in Figure 5.8 reflected a more power-law behavior (especially the March RTD) as did the observed breakthrough data. This was likely a model artifact of the well-mixed assumption in each zone (unsaturated and saturated) and model grid cell.

The simulated distributions found here were much younger than estimates based on observed stable isotope signatures [see *McGuire et al.*, submitted], which were on the order of 2 years old. There are two reasons for this discrepancy 1) the stable isotope

estimates largely reflected baseflow conditions (due to the runoff sampling routine), whereas this direct simulation approach incorporated the storm dynamics and 2) the mixing volume of our model did not include sources other than the regolith (i.e., no bedrock contribution). These observations reveal the need for future studies to incorporate bedrock contributions within catchment models that predict solute response and residence time investigations that include variable flow conditions.

### 5.5.3 *On the Value of Integrating Tracer Experiments with Hydrologic Models*

Since many catchment and hillslope scale applications require predictions concerning water quality, representing realistic residence time distributions and storage in hydrologic models is important. As demonstrated in this study by the high runoff efficiency achieved when only runoff was used to evaluate model performance, the best fitting model is not necessarily consistent with the internal process behavior. Applied tracer experiments offer an additional data source, which by nature, integrates heterogeneity into the tracer breakthrough. The breakthrough curve, like a hydrograph, reflects all of the physical process complexity into one signal and thus, provides an ideal source of information that helps constrain parameterizations and reduce model uncertainty. Then, as shown in this study, a model calibrated to tracer data can be used to explore residence time distributions, which describe how potential contaminants and solutes are retained within a catchment or hillslope. Furthermore, the modeled residence time distribution can be drawn on to better understand the limitations of model structures and to independently assess the need to incorporate (or reject) additional process detail or heterogeneity as discussed in the previous section.

## **5.6 Conclusions**

We argue that the combination of the tracer experiment, modeling exercise, and residence time simulation provides a more integrated approach to investigate runoff processes. These techniques helped to simplify observed process complexity and evaluate dominant physical processes used to structure the model. We presented a simple, spatially-explicit hydrologic model in order to identify the dominant processes necessary to explain both water and solute flux at the hillslope scale. This was accomplished by testing the model with a line-source tracer experiment, which improved parameter uncertainty, even though the overall model performance based on the fit to the runoff data decreased. The model was then used as an exploratory tool to infer potential residence time distributions that in turn assisted in the assessment of our model structure. The subsurface volume, the mixing assumption, and the water table dynamics were all found to be important controls on the distribution of residence times and potential areas of improvement within our model framework. Further model improvements by including other data sources (e.g., groundwater levels) and developing more efficient computer code to run comprehensive uncertainty analyses are currently underway.

## **5.7 Acknowledgments**

This work was supported through funding from the National Science Foundation (grant DEB 021-8088 to the Long-Term Ecological Research Program at the H. J. Andrews Experimental Forest) and Department of Forest Engineering at Oregon State University. We thank J. Moreau for assistance in providing power and datalogging

capability at the field site, C. Luce for performing the bromide analysis, and B.

Morrisette for assistance in the field and lab. We also thank R. D. Harr and D. Ranken for initiating the hillslope studies at WS10.

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Table 5.1. Model parameter description, data limits, values used in simulations.

Parameter	Description	Data		Model Parameter Sets	
		Lower limit	Upper limit	Model 1 <sup>a</sup> (uncertainty <sup>b</sup> )	Model 2 <sup>a*</sup> (uncertainty)
$n$	Average soil porosity	0.42	0.56	0.58 (25%)	0.41 (34%)
$b$ [m]	Shape factor for drainable porosity function	1	2	1.61 (34%)	1.50 (34%)
$n_0$	Surface drainable porosity	0.17	0.30	0.20 (48%)	0.20 (36%)
$f$ [m]	Shape factor for hydraulic conductivity function	0.5	0.8	0.66 (30%)	0.80 (13%)
$k_0$ [m h <sup>-1</sup> ]	Surface hydraulic conductivity	4.4	9	8.84 (42%)	6.67 (25%)
$c$	Recharge power coefficient	23 <sup>†</sup>	114 <sup>†</sup>	75.2 (41%)	44.9 (71%)
$\beta$	Bypass power coefficient	—	—	13.5 (68%)	10.4 (80%)
$n_{eff}$	Effective porosity coefficient	—	—	— —	0.55 (46%)

<sup>a</sup>Best parameter sets determined by fit to runoff (model 1) and mass flux (model 2) observed data, respectively. Model 1 efficiencies were 0.92 and 0.19 and model 2 efficiencies were 0.84 and 0.59 for runoff and mass flux, respectively.

<sup>b</sup>Uncertainty is defined as range between the 0.1 and 0.9 percentile divided by the median for the top 20% performing (i.e. based on  $E$ ) parameter values.

<sup>†</sup>Estimated using the *Brooks and Corey* [1964] pore-size distribution index

\*Selected parameter set for residence time model scenarios.

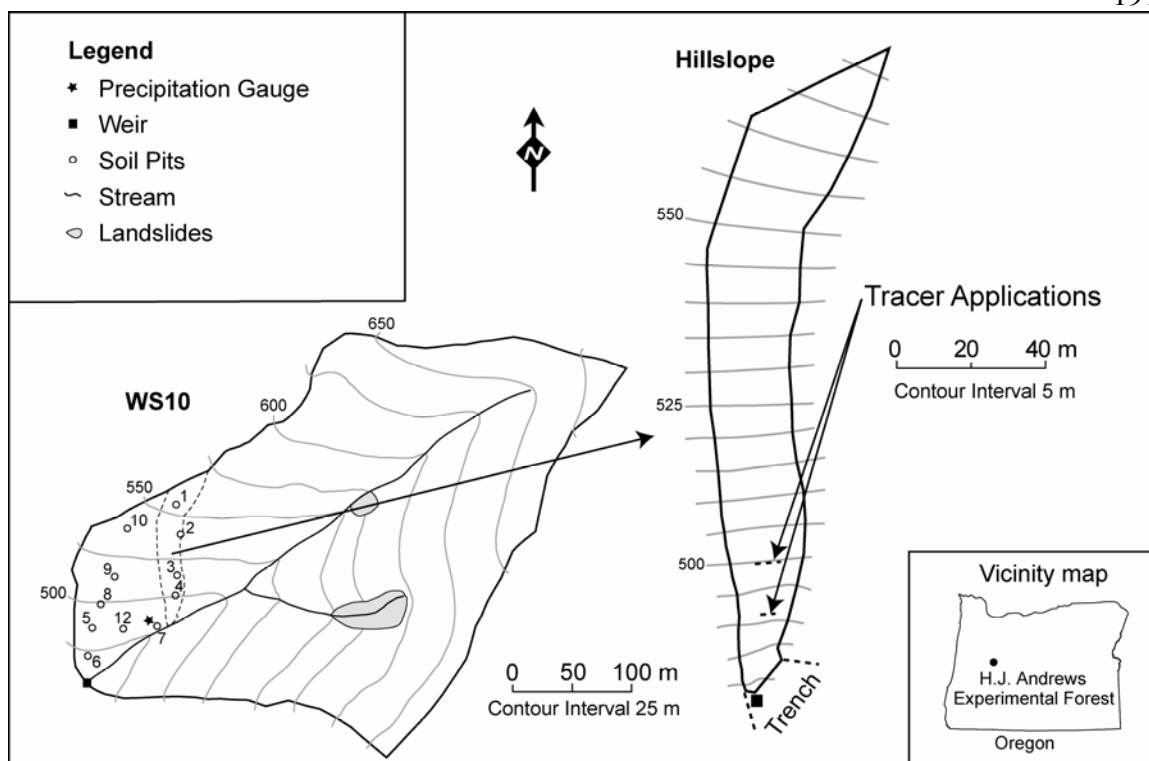


Figure 5.1. Map of the study area.

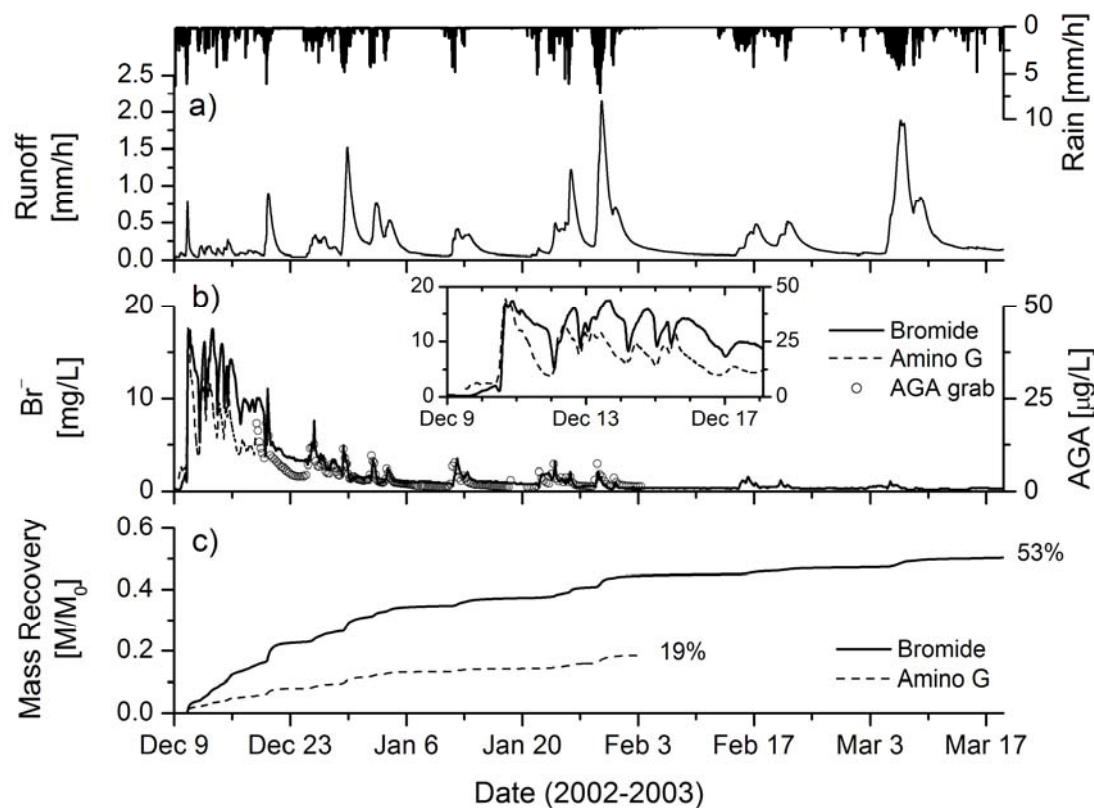


Figure 5.2. Time series of observed rainfall and runoff (a), breakthrough of bromide and Amino G acid (AGA) (b), and tracer mass recovery (c). Bromide and AGA were sampled continuously from 9 Dec. 2002; however, beginning on 19 Dec., grab samples were collected at 4 to 7 hour intervals for AGA until 4 Feb. 2003 when concentrations were at or below background levels. The first 9 days of breakthrough (b) are expanded in the inset figure and the beginning of the x-axis indicates the start of the experiment (9 Dec. 2002 21:30).

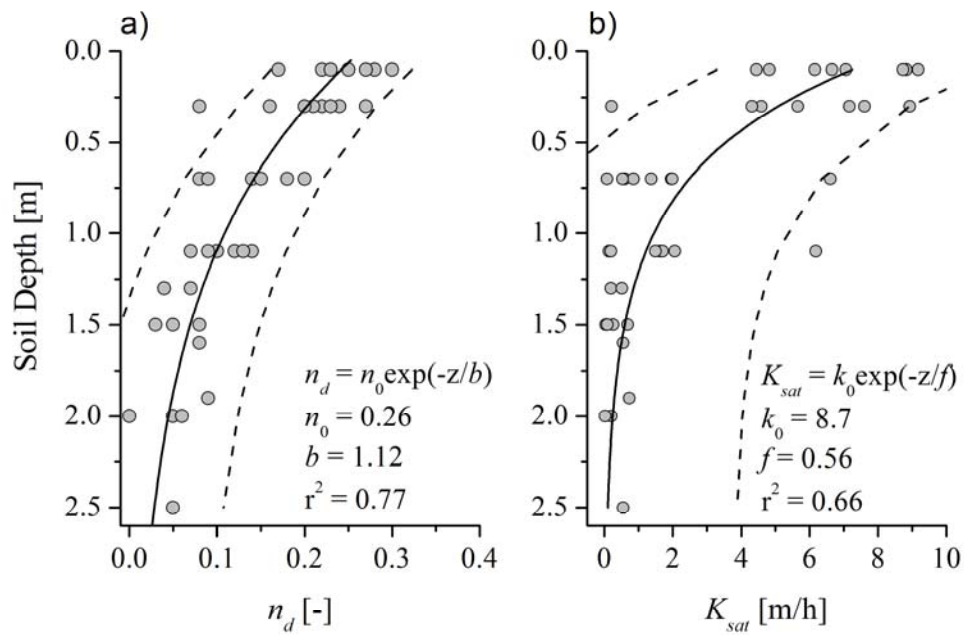


Figure 5.3. Measured saturated hydraulic conductivity ( $K_{sat}$ ) and drainable porosity ( $n_d$ ) from soil pits shown in Figure 5.1 [Ranken, 1974] fit to exponential functions (solid line). Drainable porosity is taken as the difference in volumetric water content between saturation and 100 cm of tension. Each point represents the mean of six cores and the dashed lines are the 95% prediction limits.



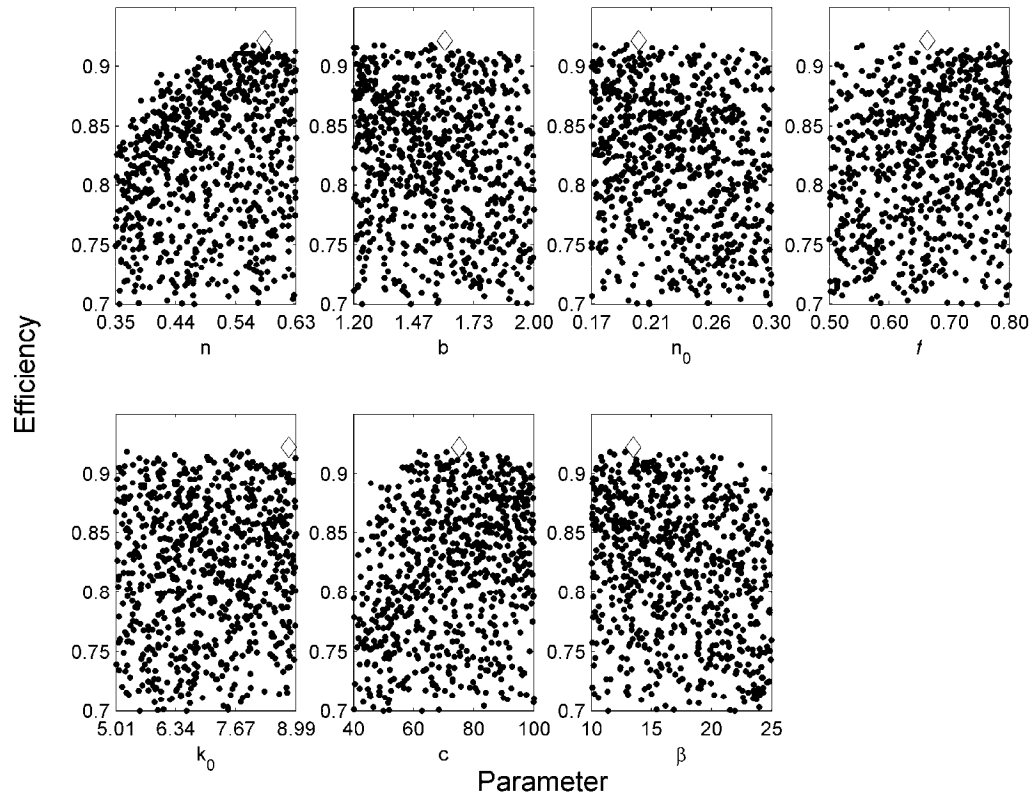


Figure 5.4. A scattergram of 1000 Monte Carlo model simulations, where each point represents one model run with different randomly selected parameters within the range shown by the x-axes and its associated Nash-Sutcliffe efficiency [1970] for runoff. The large diamonds indicates the best parameter set for runoff.

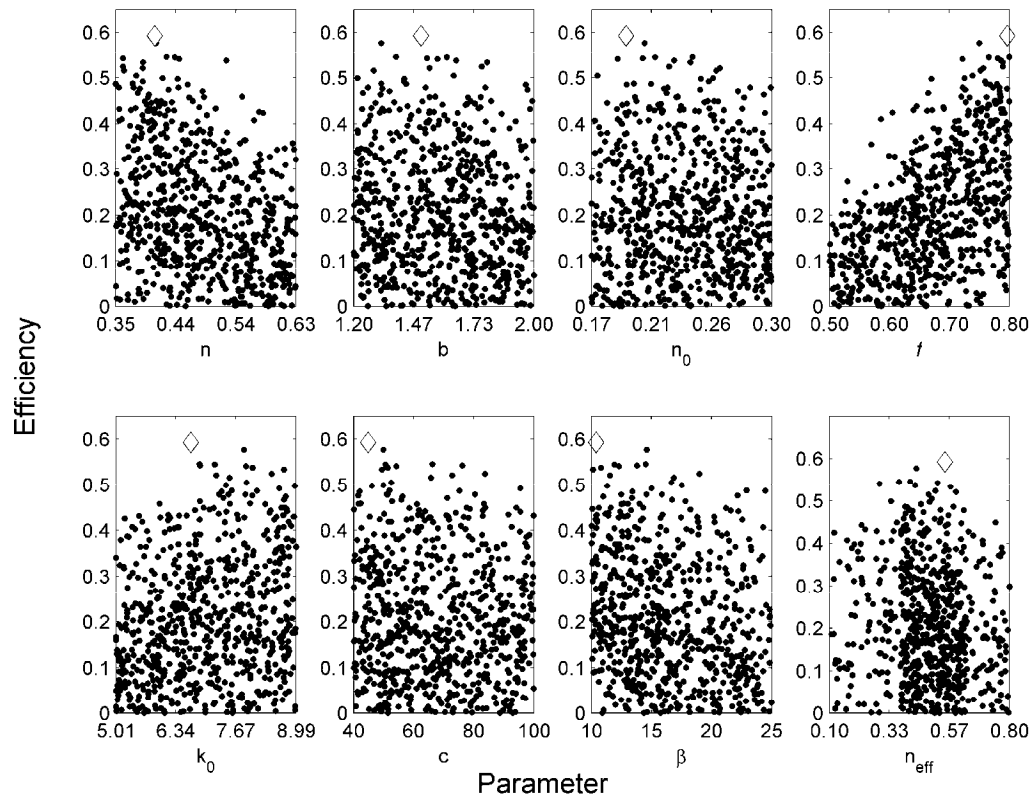


Figure 5.5. A scattergram of 1000 Monte Carlo model simulations, where each point represents one model run with different randomly selected parameters within the range shown by the x-axes and its associated Nash-Sutcliffe efficiency [1970] for mass flux. The large diamonds indicates the best parameter set for mass flux. Density changes in the  $n_{eff}$  resulted from expanding the parameter range during the Monte Carlo.

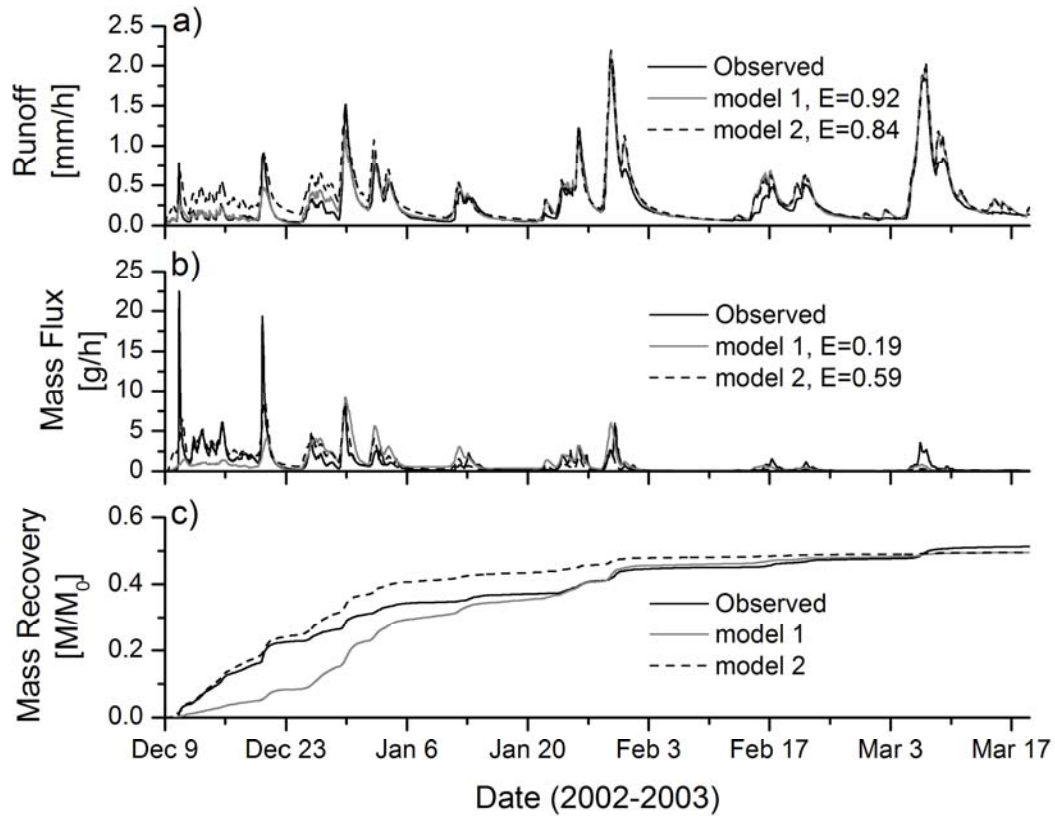


Figure 5.6. Observed (solid black line) and simulated runoff (a), line-source tracer breakthrough as mass flux (b), and mass recovery (c). Gray lines indicate the best model fit to the observed runoff data (model 1) and dashed lines indicate the best model fit to the observed mass flux data (model 2). Nash-Sutcliffe efficiencies ( $E$ ) [Nash and Sutcliffe, 1970] describing the goodness-of-fit are shown. The final mass recovery for both simulations was 50% and observed mass recovery was 53%.

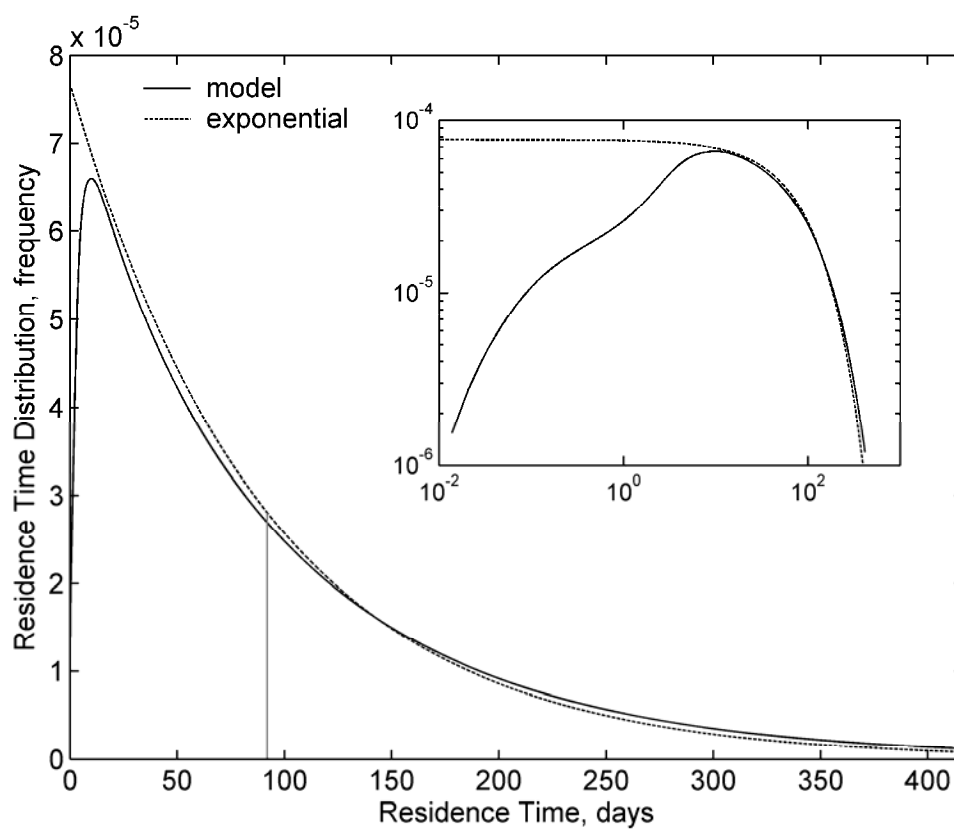


Figure 5.7. Simulated residence time distribution (solid black line) for steady-state conditions compared to an exponential distribution (dashed line). The vertical gray line shows the mean residence time for both distributions (92 days) and the inset plot shows the same distributions with logarithmic axes.

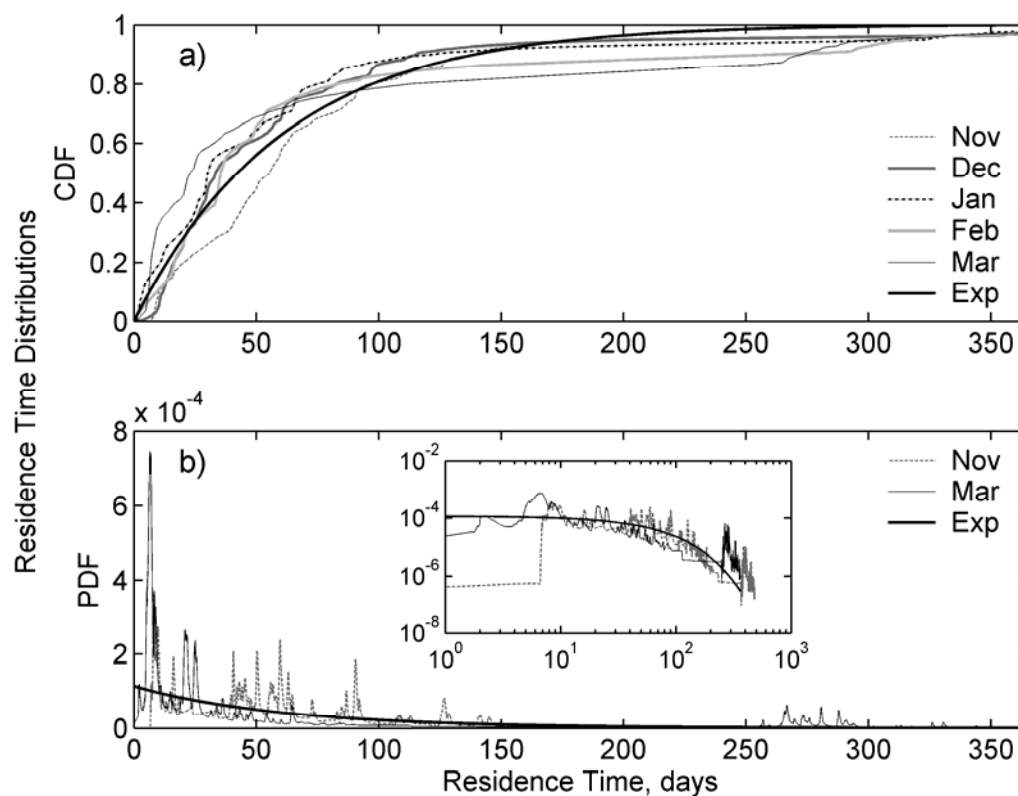


Figure 5.8. Simulated residence time distributions for non-steady-state conditions compared to an exponential distribution (heavy solid black line). The residence time distributions are shown as cumulative density functions (CDFs) (a) and select residence time distributions (Nov and Mar) are shown as probability density functions (PDFs) (b). The inset plot shows the PDFs on logarithmic axes.

## **6 Conclusions**

## **6.1 Concluding Remarks**

In recent commentaries on the state-of-the-art of hydrological science, hydrologists advocated for simplifying process complexity observed at hillslope scales into scaleable concepts that remain descriptive of their dominant physical processes at catchment scales [Blöschl, 2001; Savenije, 2001; Sivapalan, 2003; Sivakumar, 2004]. This study has attempted to illuminate the “black-box” of catchments by providing an improved understanding of the catchment-scale residence time distribution. This was achieved through the use of combined hydrometric, isotopic, and applied tracer field approaches integrated with simple interpretative models at the hillslope and multiple catchment scales.

A formal clarification on the assumptions, limitations, and methodologies used in residence time models was presented in Chapter 2. This review highlighted problems associated with tracer measurements (i.e., the length of data records and precipitation and stream sampling issues), characterizing recharge, and selecting and evaluating potential residence time distributions in catchments, especially in large-scale basins. Perhaps the most important finding of this review was the lack of techniques available to evaluate and estimate the residence time distribution at the catchment scale. Most of the approaches used to date in the catchment literature have been borrowed from groundwater investigations. These approaches do not include processes that relate to variable flow and recharge conditions that are common in catchments. The review motivated the dual approach of investigating residence time at multiple catchments of different basin size (chapter 3) and the more detailed study of hydrological processes at the hillslope and small catchment scales (chapters 4 and 5).

Chapter 3 demonstrated that residence time provides a way to aggregate complex processes across scale. Until now, residence time has been examined generally in one or two basins and little effort has been made to examine the process controls on the shape and scale of the distribution of residence times at multiple catchments. During baseflow conditions, mean residence times at the H.J. Andrews varied from 0.8 to 3.3 years in basins that ranged from 0.085 to 62.4 km<sup>2</sup>. These sites represented diverse geologic and geomorphic conditions. The relationship between residence time and basin area was tested, but was not significant. However, very strong relationships between mean residence time and simple terrain indices emerged based on flow path distance and gradient measures. This suggested that landscape organization (i.e., topography), as opposed to basin size, controlled catchment-scale transport. Results from this study may also 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 baseflow residence time. These findings may present new opportunities for catchment classification and regionalization based on simple internal topographic descriptors.

When more detailed hydrological processes were examined at the hillslope scale through a wet-up period, a conceptual model controlled largely by moisture thresholds and expanding subsurface saturated areas became apparent. The lower trenched hillslope became hydrologically connected with upslope areas as soil moisture conditions increased. Hillslope and WS10 catchment connections did not respond linearly; rather they reflected changing storage effects resulting in threshold and hysteretic patterns. During the wettest conditions, the rapid breakthrough of applied tracers and rain water



residence time distributions indicated relatively short response times of rain water that contributed runoff at the timescale of a single storm event. However, older pre-event water dominated stormflow and the residence times of soil water (10-25 d), seepage emanating from the hillslope (1-2 y), and catchment baseflow (1-2 y) based on stable isotope data were much older. These results suggest that the age of runoff during storms is an amalgamation of these various components, which changed dynamically through the wet-up season.

Modeling results from the coupled hydrologic-tracer model and field tracer experiment revealed potential residence time distributions that varied considerably with different wetness conditions. In general, the directly simulated residence times were significantly shorter than estimated residence times based on the stable isotope methods. The stable isotope estimates largely reflected baseflow conditions (due to the times when samples were taken); whereas, the direct simulation approach incorporated storm dynamics yielding a residence time distribution representing the integration of event and between-event flow processes. This study suggested that the direct simulation of residence time distributions is useful for evaluating catchment models and exploring the process controls on the residence time distribution.

Overall, this dissertation demonstrates that water residence time provides insight to hydrological processes from hillslope to large catchment scales. The residence time distribution of catchments provides a useful description of the integrated response of the diverse flow pathways in a catchment, which helps illuminate processes that control subsurface flow and transport at the catchment-scale.

## 6.2 *Implications and Related Future Work*

This work has several important implications for catchment hydrology. First, the contribution of groundwater or deep runoff sources cannot be neglected in conceptual or predictive models of runoff generation. Residence times found in several catchments in this study suggest that sources of water exceed the storage capacity of soils, indicating that deeper sources are important contributions to runoff generation. The variable contribution of groundwater end-members was not addressed in this study and presents a fruitful area for future research in the western Cascades, which are generally assumed to be dominated by shallow flow processes [e.g., *Tague and Grant, 2004*].

Second, incorporating catchment-scale residence time estimates into structuring, evaluating, and testing hydrologic models has enormous potential, especially as the hydrologic community moves toward meso- and large-scale basin modeling. By definition, the residence time is related to total catchment storage (see chapter 2) and thus, it may be used to constrain or even parameterize storage terms in catchment hydrologic models. However, this requires resolving the difference between dynamic and total storage at the catchment scale, which continues to be a major challenge in hydrology. This challenge is essentially the old water paradox, where catchments store water for weeks or months, but release it rapidly in minutes or hours in response to rainfall inputs [see *Kirchner, 2003*]. Chapter 4 would suggest that new stores are activated, according to antecedent wetness conditions and storm size, each with their own characteristic response, internal mixing dynamics, and residence time [see also *McDonnell, 2003*]. The derivation of new residence time distributions at the catchment scale may also help with this endeavor, but will require tracer signals that are not limited

by the sample frequency of typical catchment-scale tracer datasets [e.g., *Kirchner et al.*, 2000].

Finally, as demonstrated in chapter 3, catchment residence time may provide opportunities for developing scaling relationships that reflect large-scale process controls on water and solute transport. This was one of the first studies to relate residence time to topographic attributes and thus, ought to be explored in other basins with different geomorphic and climate regimes. Also, incorporating field-based residence time studies with scaling theories may provide new and important insights that are currently not possible under the predominant theoretical paradigm of scaling research [*Blöschl*, 2001].

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