# Do time-variable tracers aid the evaluation of hydrological model structure? A multimodel approach

Hilary McMillan,[1] Doerthe Tetzlaff,[2] Martyn Clark,[3] and Chris Soulsby[2]

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[1] In this paper we explore the use of time-variable tracer data as a complementary tool for model structure evaluation. We augment the modular rainfall-runoff modeling framework FUSE (Framework for Understanding Structural Errors) with the ability to track the age distribution of water in all model stores and fluxes. We therefore gain the novel ability to compare tracer/water age signatures measured in a catchment with those predicted using hydrological models built from components based on four existing popular models. Key modeling decisions available in FUSE are evaluated against streamflow tracer dynamics using weekly observations of tracer concentration which reflect the tracer transit time distribution (TTD). Model structure choice is shown to have a significant effect on simulated water age characteristics, even when simulated flow series are very similar. We show that for a Scottish case study catchment, careful selection of model structure enables good predictions of both streamflow and tracer dynamics. We then use FUSE as a hypothesis testing tool to understand how different model characterization of TTDs and mean transit times affect multicriteria model performance. We demonstrate the importance of time variation in TTDs in simulating water movement along fast flow pathways, and investigate sensitivity of the models to assumptions about our ability to sample fast, near-surface flow.

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## 1. Introduction

[2] A wide range of lumped, conceptual, rainfall-runoff model structures are currently used for hydrological modeling applications [e.g., *Singh*, 1995]. The model parameters are typically set by calibration which continues to be an important research strand within hydrology [e.g., *Kavetski et al.*, 2011; *McMillan and Clark*, 2009; *Reichert and Mieleitner*, 2009]. However, a current shift in thinking is leading the hydrological community to re-emphasize the importance of model structure over and above model calibration [*Beven*, 2010; *Clark et al.*, 2011b; *Krueger et al.*, 2010; *Savenije*, 2009; *Sivapalan*, 2009]. Model structure is critical because if model representations of the dominant runoff generation mechanisms of a catchment are not consistent with reality, the predictive power of the model may be reduced, especially outside the range of calibration conditions [*Kirchner*, 2006].

[3] The challenge of selecting appropriate model structure for a given catchment is substantial. Aggregated performance measures such as the Nash-Sutcliffe may fail to distinguish between model structures [*Clark et al.*, 2008]. This may be due to the compression of the error series into a single-valued measure [*Gupta et al.*, 2008; *Schaefli and Gupta*, 2007], to the choice of performance measure which may be sensitive to model structural complexity [e.g., *Akaike*, 1974], or to flexibility in parameterization meaning that very similar flow predictions may be obtained from multiple model structures. Multiresponse data have the potential to reduce ambiguity between competing model structures via evaluation of individual model components. This was shown in diagnostic tests proposed recently by *McMillan et al.* [2011] and *Clark et al.* [2011a], building on the concept of diagnostic signatures for model evaluation [*Gupta et al.*, 2008] and previous research into the benefits of auxiliary data to improve process understanding [e.g., *Fenicia et al.*, 2007, 2008; *Seibert and McDonnell*, 2002; *Son and Sivapalan*, 2007]. Further challenges to selecting model structure include the common finding that increased model complexity is needed as extra data sources become available for evaluation [*Vache and McDonnell*, 2006] and the inability of standard data sources of rainfall and flow to discriminate between some aspects of model structure.

[4] In this paper we explore the use of environmental tracer data as a complementary response data set for model structure evaluation. Tracers are used to investigate geographical source areas and runoff pathways [e.g., *Bergstrom et al.*, 1985; *Rodgers et al.*, 2005a; *Soulsby et al.*, 2003; *Soulsby et al.*, 2006; *Tetzlaff et al.*, 2007b]. Diagnostic tests using hydrometric data in conjunction with time domain or geographic source tracers, offer an alternative view on model performance [*Birkel et al.*, 2011a, 2011b; *Botter et al.*,

[1]National Institute of Water and Atmospheric Research, Christchurch, New Zealand.
[2]Northern Rivers Institute, School of Geosciences, University of Aberdeen, Aberdeen, UK.
[3]National Center for Atmospheric Research, Boulder, Colorado, USA.


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2008; *Iorgulescu et al.*, 2005]. For example, *Uhlenbrook and Leibundgut* [2002] carried out a multiresponse validation of a process-orientated catchment model, using measured runoff together with silica, $^{18}$O, tritium, and CFC tracers, and showed how the auxiliary data sources enabled a more realistic conceptualization of runoff generation in their catchment. An important additional benefit of validating a hydrological model against both flow and tracer dynamics is that it could be used for integrated water quantity and quality applications [*Krueger et al.*, 2009].

[5] When evaluating a hydrological model using environmental tracer data, two characterizations of transit time, i.e., the time water spends traveling through a catchment to the stream, are commonly used for comparison. These are the mean transit time (MTT) and the transit time distribution (TTD) of the tracer (which is assumed to be identical to that of the water). The TTD is the probability density function (pdf) of the time taken for water (or tracer) falling at a given moment to exit the catchment (i.e., the breakthrough curve). The MTT is the mean of this distribution. Estimates of MTT from observed data rely on an underlying model of tracer transport, often a simple prespecified time-invariant TTD with calibrated parameters. Popular distributions include gamma, exponential, or exponential-piston flow; a review is given by *McGuire and McDonnell* [2006]. The gamma distribution with shape parameter $\approx$0.5 has been shown to be appropriate for many catchments by analysis of the power spectra of conservative tracers in rainfall and streamflow [*Godsey et al.*, 2010; *Kirchner et al.*, 2000], implying the general need for a more peaked initial response and more sustained tail than a exponential distribution, i.e., as derived from a completely mixed reservoir.

[6] For two reasons, the approach of a prespecified time-invariant transit time distribution has recently been put under scrutiny. First, work by *Rinaldo et al.* [2011, 2006] and *Botter et al.* [2011] has emphasized the differences between water ages in different storages and fluxes in a generalized theoretical model of a catchment, leading to inherent time variation in TTDs. Second, *Beven* [2010] highlighted the need to apply a hypothesis testing framework to the estimation of TTDs and not to assume a particular form without evidence. Working within a multimodeling framework allows exploration of these assumptions. The model performance can be evaluated using the tracer concentrations in the stream, requiring the model to reproduce the observed tracer dynamics, with the assessment made either graphically or using a performance measure [*Fenicia et al.*, 2010; *Vache and McDonnell*, 2006]. The model simulations can then be used to derive and investigate the MTT, the shape of the TTD, and its variation with time and catchment wetness conditions. These characteristics can also be compared to possible TTD shapes and previous estimates of the MTT.

[7] In this study we augment the modular modeling system FUSE (Framework for Understanding Structural Errors) [*Clark et al.*, 2008] with the ability to track the age distribution of water in all model storages and fluxes. FUSE is a rainfall-runoff model building toolkit which allows the user to investigate hydrological modeling decisions, in particular the choice of state variables and flux equations to simulate water flow through a catchment. A complete model can be constructed with components based on well-known rainfall-runoff models: ARNO/VIC [*Wood et al.*, 1992], PRMS [*Leavesley et al.*, 1983], Sacramento [*Burnash et al.*, 1973], and Topmodel [*Beven and Kirkby*, 1979]. The FUSE concept is designed to allow testing of competing modeling hypotheses of similar complexity but alternative structures, with individual control of each model component allowing systematic testing. We therefore gain the novel ability to track conservative tracers and compare tracer/water transit time signatures measured in a catchment with predictions made using this flexible modeling system. Our aims are as follows: (1) To compare the ability of competing model structures to predict stream tracer response, while retaining similar streamflow behavior. (2) To use the FUSE models as a tool to explore how different model characterizations of TTDs and MTTs (including time variability) affect model behavior and multicriteria model performance. (3) To use sensitivity analyses to show how simulated tracer response is affected by the interaction of model structure with parameter values and mixing assumptions.

## 2. Study Site

### 2.1. Catchment Characteristics

[8] The Loch Ard Burn 10 (B10) catchment (0.9 km$^2$) lies in the Central Scottish Highlands (Figure 1), and was chosen due to availability of long-term hydrochemical tracer data. Average annual precipitation is 1980 mm and average runoff is 1660 mm. Slopes are gentle (generally less than 10°) and mean elevation is 170 m. The catchment is forested with plantations of Sitka Spruce (*Pitea Sitchensis*). Forest operations occurred between 1990 and 2002 with 39% of forest cover felled, however there is little evidence for any major change in average or high flows after the felling [*Tetzlaff et al.*, 2007a]. The geology is dominated by low permeability metamorphic rocks [*Miller et al.*, 1990]; bedrock outcrops occur on interfluves of the steep northwestern slopes. The most common soils are thin, poorly drained minerogenic gleyed soils.

[9] Runoff generation processes are relatively well understood in the catchment [*Dawson et al.*, 2008; *Hrachowitz et al.*, 2009a; *Tetzlaff et al.*, 2010; *Tetzlaff et al.*, 2007a]. The catchment is highly responsive, with low base flow levels compared to stormflow (the ratio of low flows to flood flows may be up to 10$^4$) [*Tetzlaff et al.*, 2007a]. The catchment maintains low soil moisture deficits and most parts of the catchment are highly connected to the stream network via a series of drainage ditches and saturated riparian zones, leading to high runoff rainfall ratios (varying between 0.64 and 0.98 [*Dawson et al.*, 2008]). Storm runoff is thought to be dominated by flow paths in the upper soil horizons, influenced by high vertical gradients in the saturated hydraulic conductivity of the soil. Conductivity was found to vary from 0.3 cm h$^{-1}$ in lower layers to 600 cm h$^{-1}$ in surface layers in similar forested gley soils elsewhere [*Soulsby and Reynolds*, 1993]. However tree roots and areas of exposed bedrock provide pathways to fracture systems in the bedrock, allowing some deeper recharge to occur [*Tetzlaff et al.*, 2010]. Although hydrograph separations based on stream alkalinity are uncertain, average groundwater contributions to annual streamflow were estimated to be in the range 35%–47%.

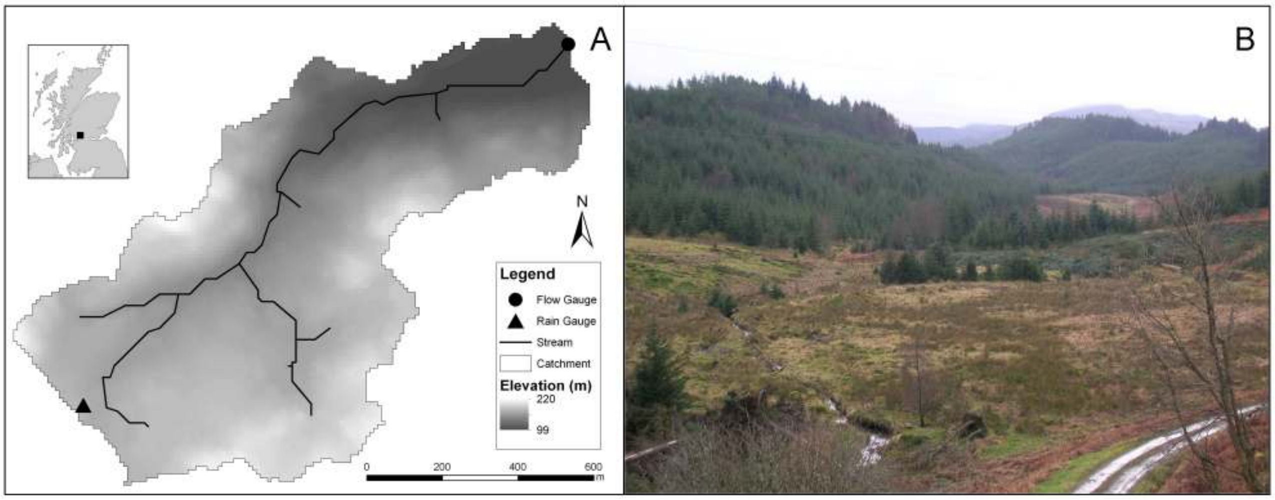


**Figure 1.** (a) Loch Ard B10 catchment map and instrument locations. (b) Photograph of Loch Ard B10 catchment.

## 2.2. Hydrometric Data

[10] Daily rainfall totals were available using records from three gauges close to the catchment. Due to the flashy nature of the small catchment, rainfall totals at a subdaily time step were required in order to capture the fast runoff generation mechanisms and ensure correct timing of runoff in the model. Hourly rainfall data was available from four stations (Sloy, Loch Venachar, Abbotsinch, and Bishopton) at 18 to 30 km from Loch Ard. The hourly data were expressed as a fraction of daily precipitation total at each hourly station, and the hourly ratios were interpolated (using inverse distance weighting) to the basin centroid. This timing information was then used to disaggregate the daily rainfall totals. Potential evapotranspiration (PET) was calculated based on daily temperature data using the Hamon method which is recommended for cases where radiation data is not available [*Lu et al.*, 2005]. Flow data has been collected since 1989 using a concrete crump weir maintained by the Scottish Environment Protection Agency (SEPA). Flow data was extracted at a daily time step from the UK National River Flow Archive.

## 2.3. Hydrochemical Data

[11] During the period 1990–2002, a consistent set of hydrochemical data including weekly precipitation and streamflow samples was available, and hence this time period was used for analysis (Figure 2). The precipitation samples (collected using open funnel bulk deposition samplers) and streamflow dip samples were filtered through a 0.45 μm polycarbonate membrane filter. Ion chromatography was

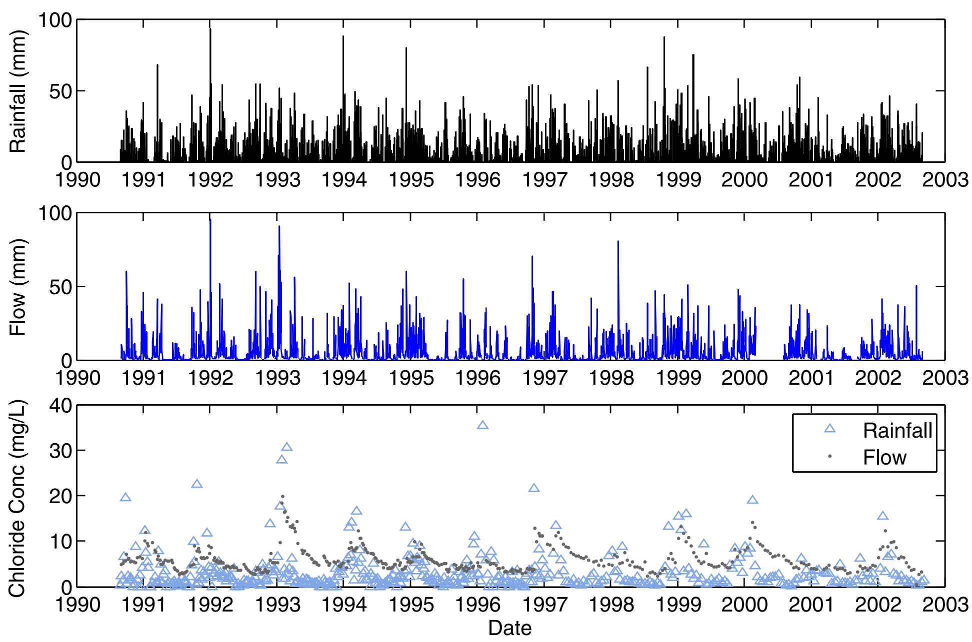


**Figure 2.** Hydrometric and hydrochemical data available for the Loch Ard B10 catchment.

then used to determine chloride ($Cl^-$) concentrations. Chloride quantities in the catchment are increased due to dry and occult deposition, and hence the input concentrations were rescaled to ensure mass balance using an adjustment factor, assumed constant with time. Some previous studies suggest a range of models of dry and occult deposition including dependence on wind speed, wind direction, and land use changes [e.g., *Page et al.*, 2007; *Oda et al.*, 2009]. However, in the Atlantic-maritime Scottish context, dry and occult deposition is generally highest when sea-salt concentrations in the atmosphere are highest, which is also when wet deposition tends to be highest, hence a constant correction is a reasonable assumption. *Kirchner et al.* [2010] showed that when using a constant correction assumption in Scottish catchments, the use of chloride versus isotope tracers led to consistent process identification, and therefore concluded that the unmodeled depositional processes do not materially affect inferences drawn from the data. For further details on the hydrochemical data collection, processing, and mass balance adjustment refer to *Hrachowitz et al.* [2009a].

## 3. Methods

### 3.1. Tracking Water Through Hydrological Models

[12] This paper uses the FUSE multimodel framework to enable individual control of hydrological model components, based on a variety of popular models. The modeling choices available include the choice of state variables in the unsaturated and saturated zones, and the choice of flux equations for surface runoff, interflow, vertical drainage, base flow, and evaporation. In order to compare modeled and measured tracer dynamics, in addition to flow dynamics, capability was added to the models to simulate routing and transit times of individual water "parcels" through conceptual model stores.

[13] We identified two possible strategies to achieve this capability, distinguished by the additional state variables used to track water movement. The first strategy uses state variables which quantify tracer concentrations in each conceptual store. The evolution of tracer concentration is controlled by input precipitation depth and tracer concentration, and flux equations describing tracer movement between storages. This is the method most commonly used in previous studies which integrate tracer information into hydrological models [e.g., *Birkel et al.*, 2010; *Birkel et al.*, 2011b; *Dunn et al.*, 2010; *Fenicia et al.*, 2010; *Vache and McDonnell*, 2006].

[14] The second strategy uses state variables which quantify the distribution of water ages (defined as the elapsed time since a particle of water fell as rainfall) in each store, at a given time (i.e., the state variables are multidimensional and specify an empirical histogram of water ages). The evolution of the distributions is controlled by input precipitation depths, aging of the water in each store, and flux equations describing water movement between stores. This strategy is a generalization of the previous method, as tracer concentrations in any store or flux can be directly calculated using convolution of the water age distribution with the corresponding input tracer concentrations (Figure 3). It also allows additional information to be easily derived such as mean and shape of the simulated water age distribution. This strategy relies on the underlying equations for conservative

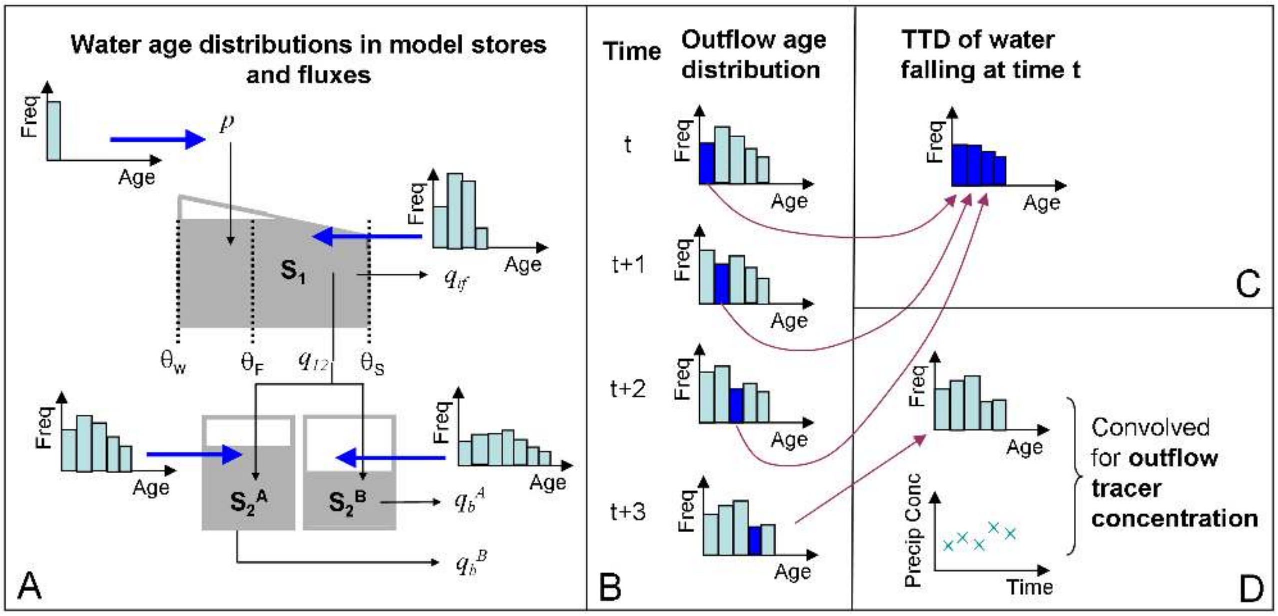


**Figure 3.** Conceptual diagram showing process used to calculated model TTDs and outflow tracer concentrations in a sample FUSE model. (a) Water age distribution of each reservoir ($S_1$ upper zone, $S_2^{A,B}$ lower zone) stored as histogram. Fluxes ($p$ precipitation, $q_{if}$ interflow, $q_{12}$ drainage, $q_b^{A,B}$ base flow) have the age signature of their source reservoir. (b) Outflow age distribution for time $t$ is the sum of distributions from component fluxes ($q_{if}$, $q_b^{A,B}$). (c) TTD of input water is calculated from the corresponding outflow times. (d) Outflow tracer concentration calculated by convolution of outflow age distribution with precipitation tracer concentrations.

tracers derived by *Botter et al.* [2010, in particular equation (17) for tracer mass flux] and summarized in *Botter et al.* [2011, Table 1]. However the numerical implementation used in this paper differs as we solve concurrently for both soil water dynamics and age distributions.

[15] An example of the implementation of the second strategy is given here for demonstration. Consider a simple model with variable $S_1$ representing water volume in the soil zone. The equation controlling evolution of $S_1$ may be as follows:

$$\frac{dS_1}{dt} = (p - q_{sx}) - e - q, \tag{1}$$

where $p$ is precipitation, $q_{sx}$ is saturation excess runoff, $e$ is evaporation, and $q$ is drainage. Now define a histogram (i.e., numerical vector representation of the pdf) $\mathbf{S_1^t}$ partitioning the volume $S_1$ by age. The equivalent differential equation for $\mathbf{S_1^t}$ is as follows:

$$\frac{d\mathbf{S_1^t}}{dt} = (\mathbf{p^t} - \mathbf{q_{sx}^t}) - \mathbf{e^t} - \mathbf{q^t}. \tag{2}$$

[16] Equation 2 relies on similar histogram distributions $\mathbf{p^t}$, $\mathbf{q_{sx}^t}$, $\mathbf{e^t}$, and $\mathbf{q^t}$ of the fluxes $p$, $q_{sx}$, $e$, and $q$. However, these histograms are known: water in rainfall ($p$) and $q_{sx}$ is all of age 1; water in $e$ and $q$ has age distributions equal to that of $\mathbf{S_1^t}$ at the start of the time step under the complete mixing assumption (refer to section 3.3 on mixing assumptions), and the magnitude of these fluxes is given by the model equations. Therefore equation (2) can be solved for $\mathbf{S_1^t}$ at the next time step. The same strategy can be used for each model state equation, giving a complete solution for water age evolution in each store and flux. Finally, the method requires an initial histogram form (exactly as an initial value for all model states is required). A uniform distribution is used, followed by a spin up period as for the other model states.

[17] In this study the second strategy was preferred for its generality. An important aim of the study is to understand how different model characterizations of MTTs and TTDs affect model performance, and this information can be estimated more completely using the second method (see section 3.2 for description of the relationship between TTD and water age). Hence, the additional capability was added to a FUSE prototype.

### 3.2. Model Output

[18] The water-tracking model framework was designed to allow output of various aspects of simulated water age and transit times. Time series of the model state variables provide the age distribution in all stores, at each time step (1 day increments were used here, matching the flow data resolution, but the time step could be varied). Age distributions of all fluxes, including the catchment outlet flow, are also calculated. Time-varying statistics of the distributions, e.g., mean water age, can easily be derived. The TTD is calculated for each time step in a secondary step which links each input quantity of rainfall to its age at the time it exited the catchment as streamflow. The TTD depends on both antecedent and current catchment wetness conditions, which determine how quickly water is driven through the catchment system. The TTDs may also be averaged over all time steps to create a "master TTD" [*Botter et al.*, 2011; *Rinaldo et al.*, 2011]. The tracer volume or flux is given by the convolution of the water age distribution with the time series of input tracer concentrations. The model can be evaluated by its ability to simulate tracer dynamics by direct comparison of modeled and measured tracer outflow concentrations. This is a more direct and powerful test than invoking the MTT as a comparison tool, as any calculation of MTT relies on some underlying model of TTD.

### 3.3. Mixing Assumptions

[19] Simulated water ages within a hydrological model are strongly dependent on the mixing assumptions used. Within a conceptual model store, instantaneous and complete mixing is the most usual assumption [e.g., *Fenicia et al.*, 2010; *Vache and McDonnell*, 2006]. A justification for this may be that by stipulating the store as the fundamental unit of model design, complete mixing within that store is implicit: otherwise the store would represent an amalgamation of lower-level stores in which complete mixing did occur.

[20] Recent work has however suggested that partial mixing behavior may provide a more accurate representation of observed tracer concentrations [*Barnes and Bonell*, 1996; *Dunn et al.*, 2007; *Fenicia et al.*, 2010]. Partial mixing refers to a water store in which some fraction of the volume controls hydrological response, with the remaining inert volume contributing only to tracer mixing. This concept is equivalent to a modification of the storage-discharge behavior of the water store, i.e., that no discharge occurs below some threshold. Such behavior is commonly assumed in hydrological models, e.g., that modeled percolation only occurs when soils are above field capacity (e.g., in the PRMS and Sacramento models underlying FUSE). In this study, mixing behaviors will only be changed in this way, i.e., through alternative storage-discharge parameterizations for both unsaturated and saturated model zones. The relevant model choices are as follows: In the upper zone, use of a single state variable simulates partial mixing, whereas use of split state variables simulates total mixing within the free storage reservoir. In the lower zone, the parallel linear reservoirs options simulate total mixing, but the Topmodel option simulates a hybrid method whereby discharge is greatly reduced but not zero as the volume of stored water decreases (for information on these model options refer to section 3.4 and Figure 4).

[21] An important aspect of mixing behavior is the extent to which precipitation is assumed to mix with shallow soil water before flowing into the channel as saturation excess or other overland flow representations. Although saturation excess flow might be visualized as unmixed with soil water, empirical evidence using geochemical tracers in Scottish catchments suggests that surface runoff does often partially acquire the chemical signature of soil water [*Birkel et al.*, 2011b]. If model simulation of mixing is required, its occurrence and extent must be exactly specified, possibly through introduction of calibrated parameters if sufficient process knowledge is not available. In this study, the simplest option was used whereby saturation excess flow was treated as unmixed, in common with previous studies [e.g., *Botter et al.*, 2008]. To explore the impact of this

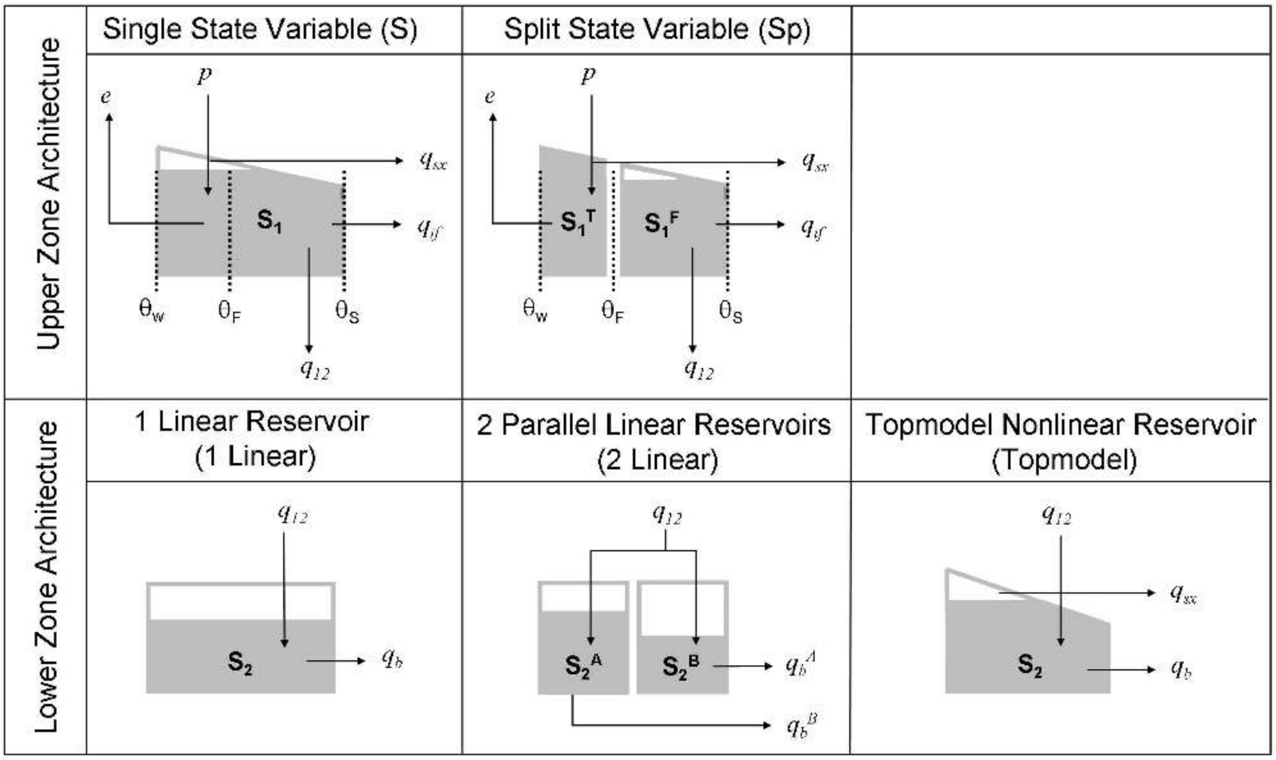


**Figure 4.** Simplified wiring diagram showing model architecture options used in this study. Upper zone: [S] a single state variable $S_1$ combining tension and free storage, [Sp] separate state variables for tension $S_1^T$ and free $S_1^F$ storage. Lower zone: [1 Linear] $S_2$ a single linear reservoir [2 Linear] $S_2^A$, $S_2^B$ two parallel linear reservoirs [Topmodel] $S_2$ a single nonlinear reservoir based on Topmodel concepts (where surface runoff $q_{sx}$ is controlled by the lower zone). Key to soil moisture values: $\theta_W$ wilting point (here 0), $\theta_F$ field capacity ($\phi \cdot S_{1,\max}$), $\theta_S$ saturation point ($S_{1,\max}$).

assumption, a sensitivity analysis was carried out to investigate the effect of flow partitioning between surface (unmixed) and subsurface (mixed) pathways (refer to section 4.5).

### 3.4. Model Implementation

[22] The FUSE framework provides hundreds of possible model combinations using different combinations of components from four popular hydrological models [*Clark et al.*, 2008]. In this study, to provide a manageable scope we investigate the effect of key decisions of upper and lower layer architecture on the simulated stream water transit time (Conceptual diagrams including the outflow pathways for each model component are shown in Figure 4.)

[23] In all cases the following decisions are treated as fixed. (a) Evapotranspiration is satisfied from the single upper soil layer: this is the simplest option available. (b) Percolation is parameterized as a linear function of upper zone storage above field capacity: again the simplest option. Note also that the alternative formulation of percolation as a power function of total upper zone storage was found to give poor results in initial trials. (c) Surface runoff is parameterized as a power function of total upper zone storage, except when using the Topmodel formulation where it is controlled directly from lower zone storage. The state and flux equations defining each of the resulting six models are given in Table 1, with fluxes defined in Table 2. The alternative choices provided for in FUSE could be investigated for their effect on transit time in future work.

[24] FUSE is formulated as a state-space model and enables several classes of time stepping schemes to control model numerical behavior [*Clark and Kavetski*, 2010; *Kavetski and Clark*, 2010]. The additional model equations required to track water age are similarly written in state-space form. The numeric scheme chosen was a fixed-step explicit Euler for simplicity, using short 15 min substeps to ensure numerical stability and accuracy. The model used input precipitation data at hourly resolution. Model flow simulations were evaluated at a daily time step, commensurate with flow data availability and which minimizes the effect of any rainfall timing errors introduced by the interpolation method used for rainfall disaggregation. In our study, evaluation at daily time step seemed sufficient to capture the flow generation processes of interest (i.e., the effect of upper and lower zone model architecture choices), and is at higher resolution than processes captured by tracer measurements which relate to (slower) water transit times rather than the subdaily dynamic response.

### 3.5. Model Parameters

[25] When comparisons are made between hydrological model structures, there is interplay between the choice of model structure and the choice of model parameters: both can influence flow and transit time predictions and each

**Table 1.** State and Flux Equations for the 6 FUSE Models Tested in This Paper

| Model | 1 (Single Upper/ 1-Linear Lower) | 2 (Single Upper/ 2-Linear Lower) | 3 (Single Upper/ Topmodel Lower) | 4 (Split Upper/ 1-Linear Lower) | 5 (Single Upper/ 2-Linear Lower) | 6 (Single Upper/ Topmodel Lower) |
|---|---|---|---|---|---|---|
| Unsaturated Zone Architecture[a] | $\frac{dS_1}{dt} = \begin{matrix}(p - q_{sx}) - e - \\ q_{12} - q_{if} - q_{ufof}\end{matrix}$ | $\frac{dS_1}{dt} = \begin{matrix}(p - q_{sx}) - e - \\ q_{12} - q_{if} - q_{ufof}\end{matrix}$ | $\frac{dS_1}{dt} = \begin{matrix}(p - q_{sx}) - e - \\ q_{12} - q_{if} - q_{ufof}\end{matrix}$ | $\frac{dS_1^T}{dt} = (p - q_{sx}) - e - q_{utof}$<br>$\frac{dS_1^F}{dt} = q_{utof} - q_{12} - q_{if} - q_{ufof}$ | $\frac{dS_1^T}{dt} = (p - q_{sx}) - e - q_{utof}$<br>$\frac{dS_1^F}{dt} = q_{utof} - q_{12} - q_{if} - q_{ufof}$ | $\frac{dS_1^T}{dt} = (p - q_{sx}) - e - q_{utof}$<br>$\frac{dS_1^F}{dt} = q_{utof} - q_{12} - q_{if} - q_{ufof}$ |
| Saturated Zone Architecture[a] | $\frac{dS_2}{dt} = q_{12} - q_b - q_{sfof}$ | $\frac{dS_2^A}{dt} = \frac{q_{12}}{2} - q_b^A - q_{sfofa}$<br>$\frac{dS_2^B}{dt} = \frac{q_{12}}{2} - q_b^B - q_{sfofb}$ | $\frac{dS_2}{dt} = q_{12} - q_b - q_{sfof}$ | $\frac{dS_2}{dt} = q_{12} - q_b - q_{sfof}$ | $\frac{dS_2^A}{dt} = \frac{q_{12}}{2} - q_b^A - q_{sfofa}$<br>$\frac{dS_2^B}{dt} = \frac{q_{12}}{2} - q_b^B - q_{sfofb}$ | $\frac{dS_2}{dt} = q_{12} - q_b - q_{sfof}$ |
| Evapotranspiration | $e = pet \cdot \min\left(\frac{S_1}{\phi \cdot S_{1\max}}, 1\right)$ | | | | | |
| Drainage | $q_{12} = k_u \cdot \left(\frac{S_1^F}{(1-\phi)S_{1\max}}\right)^c$ | | | | | |
| Interflow[b] | $q_{if} = k_i \cdot \left(\frac{S_1^F}{(1-\phi)S_{1\max}}\right)$ | | | | | |
| Baseflow[b] | $q_b = \upsilon S_2$ | $q_b = \upsilon_A S_2^A + \upsilon_B S_2^B$ | $q_b = \frac{K_s S_{2\max}}{\lambda^n n} \cdot \left(\frac{S_2}{S_{2\max}}\right)^n$ | $q_b = \upsilon S_2$ | $q_b = \upsilon_A S_2^A + \upsilon_B S_2^B$ | $q_b = \frac{K_s S_{2\max}}{\lambda^n n} \cdot \left(\frac{S_2}{S_{2\max}}\right)^n$ |
| Surface Runoff[b] | $q_{sx} = p\left(1 - \left(1 - \frac{S_1}{S_{1\max}}\right)^b\right)$ | $q_{sx} = p\left(1 - \left(1 - \frac{S_1}{S_{1\max}}\right)^b\right)$ | $q_{sx} = p\int_{\zeta_{crit}}^{\infty} f(\zeta)d\zeta$<br>$\zeta_{crit} = \lambda\left(\frac{S_2}{S_{2\max}}\right)^{-1}$ [c] | $q_{sx} = p\left(1 - \left(1 - \frac{S_1}{S_{1\max}}\right)^b\right)$ | $q_{sx} = p\left(1 - \left(1 - \frac{S_1}{S_{1\max}}\right)^b\right)$ | $q_{sx} = p\int_{\zeta_{crit}}^{\infty} f(\zeta)d\zeta$<br>$\zeta_{crit} = \lambda\left(\frac{S_2}{S_{2\max}}\right)^{-1}$ [c] |

[a]Overflows from tension ($q_{utof}$), free ($q_{qufof}$), and lower ($q_{sfof}$) reservoirs represent addition flow into the free storage, surface runoff, and baseflow, respectively. Logistic functions are used to smooth the threshold relating to the fixed storage capacities (following *Clark et al.* [2008], Section 4.8).

[b]The time delay in runoff is modeled using a gamma distribution $\Gamma(\mu,3)$ of routing times applied to all fluxes (following *Clark et al.* [2008], Section 4.9).

[c]The variable $\zeta$ for surface runoff parameterization of models 3 and 6 describes the spatial distribution of the topographic index [*Beven and Kirkby*, 1979]. The distribution used is $\Gamma(\lambda,\chi)$ fitted to data from the digital elevation model (following *Clark et al.* [2008], Section 4.6).

**Table 2.** Model Fluxes (All Units Are mm d$^{-1}$)

| Variable Name | Description |
|---|---|
| $p$ | Precipitation |
| $e$ | Evapotranspiration |
| $q_{sx}$ | Saturation excess runoff |
| $q_{if}$ | Interflow (subsurface stormflow) |
| $q_{12}$ | Drainage from upper to lower zone |
| $q_b$ $q_b^A$ $q_b^B$ | Baseflow (from single, primary, secondary reservoir) |
| $q_{utof}$ $q_{ufof}$ | Overflow from upper zone (from tension, free reservoir) |
| $q_{sfof}$ $q_{sfofa}$ $q_{sfofb}$ | Overflow from lower zone |

can compensate for deficiencies in the other, though not necessarily in agreement with reality. In this study the focus was on model structure. Therefore default parameter values for the FUSE models were used where possible, as recommended by *Clark et al.* [2011a]. Measured information or process knowledge from the Loch Ard catchment was also used to set parameter values where appropriate; this method assumes a translation from field to model scale but given the process-orientated nature of the models it was considered preferable to setting the parameters via calibration. The depth of the upper humic/peaty soil layer contributing to shallow subsurface slow is approximately 400 mm [*Tetzlaff et al.*, 2007a]; assuming a typical porosity for peat of 0.8 allows the upper store depth to be set as 320 mm. Typical field capacity for peat of 0.35 enables the fraction of total storage as tension storage to be set at 0.44 (= 0.35/0.8). Known values of the fractional groundwater contribution to streamflow were also used as "soft data" [*Seibert and McDonnell*, 2002] to guide the parameter choice. A digital terrain model (EDINA Digimap) of the catchment was used to estimate the topographic index distribution parameters required for the Topmodel component of FUSE.

[26] The remaining one or two parameters relating to the lower zone storage [storage depth, base flow exponents, base flow depletion rate(s)] were chosen using a simple calibration procedure by exhaustive search (accompanying visualization by contour plot) of model performance in relation to parameter value (Figure 5). As shown, the single linear reservoir model is not sensitive to the lower zone storage depth (this parameter only influences model predictions in the rare case that the tank fills completely) and hence this is set to infinite depth in the model (this is also true for the stores in the model with two parallel linear reservoirs). The Topmodel nonlinear reservoir model shows dependency between the lower zone storage size and base flow exponent, which could therefore be varied jointly in the model to improve tracer simulations if necessary. The dependence is indicated by the form of the base flow equation (Table 1). The same parameter sets were used for both single and split variable upper zone structures. The complete parameter sets thus derived provide a robust baseline calibration for comparisons between structures (Table 3). The fitted models all give very similar predictions of flow dynamics, with only very minor differences in the flood peaks and low recessions. Nash-Sutcliffe scores were all in the range 0.75–0.80 when validated over a 12 year period.

## 4. Results

[27] Section 4 is organized as follows. First the six different FUSE model structures (2 options for upper zone architecture $\times$ 3 options for lower zone architecture) are evaluated against the tracer measurements from the B10 catchment using direct comparison using tracer output series (section 4.1). A comparison with the results of previous studies is also made using MTTs (section 4.2).

[28] Second, we use the FUSE models as a tool for hypothesis testing by comparing characteristics of simulated TTDs and MTTs between models with differing performance. (1) Models are run in steady state (i.e., constant precipitation input) to study time-invariant representations of the TTD (section 4.3.1). (2) Models are run dynamically (i.e., measured precipitation input) to study time-varying behavior on MTT and TTD caused by seasonal/event-scale changes in wetness conditions (section 4.3.2). (3) A sensitivity analysis of effect of model calibration (section 4.4) and mixing behavior (section 4.5) on the shape of the modeled TTD.

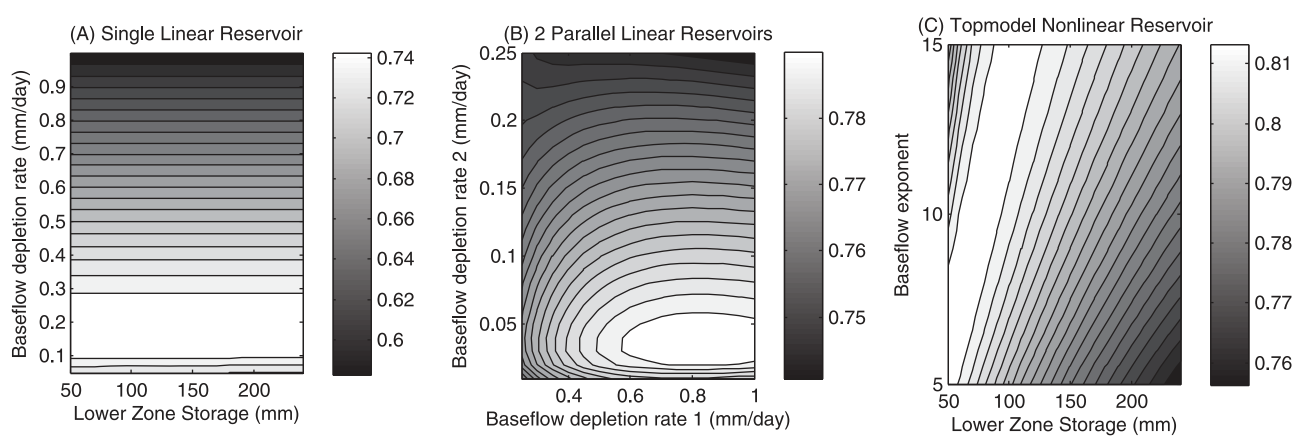


**Figure 5.** Calibration results for lower zone storage parameters for three lower zone model architectures. The objective function is the sum of squared errors between modeled and measured discharge series, after Box-Cox transformation to normalize error variance. The calibration period was over two hydrological years (1998–1999).

**Table 3.** Parameters Used for Different FUSE Models[a]

| | | Lower Zone Formulation | | | |
|---|---|---|---|---|---|
| Parameter | Description | Single Linear | Parallel Linear | Topmodel | Parameter Type |
| $S_{1,\max}$ | Maximum storage in unsaturated zone (mm) | 320.0 | 320.0 | 320.0 | Field |
| $S_{2,\max}$ | Maximum storage in saturated zone (mm) | Inf | Inf | 91.3 | Calibrate |
| $\phi$ | Fraction total storage as tension storage | 0.440 | 0.440 | 0.440 | Field |
| $k_u$ | Vertical drainage rate (mm/day) | 750.0 | 750.0 | 750.0 | Default |
| $c$ | Vertical drainage exponent | 1.0 | 1.0 | 1.0 | Default |
| $k_i$ | Interflow rate (mm/day) | 1000.0 | 1000.0 | 1000.0 | Default |
| $k_s$ | Baseflow rate (mm/day) | 1000.0 | 1000.0 | 1000.0 | Default |
| $n$ | Baseflow exponent | N/A | N/A | 12.18 | Calibrate |
| $\upsilon$ | Baseflow depletion rate (single reservoir) (/day) | 0.176 | N/A | N/A | Calibrate |
| $\upsilon_A$ | Baseflow depletion rate (primary reservoir) (/day) | N/A | 0.840 | N/A | Calibrate |
| $\upsilon_B$ | Baseflow depletion rate (secondary reservoir) (/day) | N/A | 0.0317 | N/A | Calibrate |
| $b$ | ARNO/VIC *b* exponent | 0.500 | 0.500 | 0.500 | Default |
| $\lambda$ | Mean of log topographic index distribution (m) | N/A | N/A | 5.91 | Field |
| $\chi$ | Shape parameter of topographic index distribution | N/A | N/A | 2.57 | Field |
| $\mu$ | Time delay in runoff | 0.3 | 0.3 | 0.3 | Calibrate |

[a]Parameter values are identified as [Field] identified from field knowledge, [Default] default recommended FUSE values, or [Calibrate] calibrated. Refer to section 3.5 for details.

### 4.1. Model Structure Evaluation: Output Tracer Dynamics

[29] The models were driven using measured precipitation depths and weekly precipitation chloride concentrations for the years 1990–2002. Observed chloride concentrations in stream water were then compared with the model simulations. The results are shown in Figure 6 (panels a and b), with closeups (panels c and d) of the largest peak in the tracer concentration series, from December 1992 to October 1993.

[30] Figure 6 shows the clear differences in simulated tracer response between models using single versus split upper state variables. The models using a single variable simulate greater mixing of soil water and hence a more damped tracer response, which corresponds more closely to the measured stream water chloride concentrations. The split upper state variable approach produces simulated spikes in tracer concentration (due to reduced mixing within the model leading to faster tracer breakthrough) which do not occur in the measured data. Hence to provide a model which can simulate both flow dynamics and tracer response in the Loch Ard catchment, the single state variable formulation would be the preferred choice.

[31] Within those models using the single upper state variable, the choice of lower zone formulation makes a smaller but evident difference in simulated tracer response. The single linear reservoir model simulates extended peaks of tracer concentration higher than those measured, and concentrations which are too low during recession periods. This indicates that water is routed too quickly through the model, with insufficient depth of stored water for realistic mixing behavior. The parallel linear reservoir and Topmodel formulations simulate less sustained peak concentrations which more closely match the measured values (e.g., Figure 6c). In recession periods however, the parallel linear reservoir model simulates too low concentrations, and hence this model has insufficient mixing in the lower reservoirs. The Topmodel architecture (i.e., a single nonlinear reservoir) most closely simulates tracer recession behavior, and is overall most successful in reproducing the tracer dynamics.

[32] Both the parallel linear reservoir and Topmodel architectures produce unobserved short-duration fluctuations in tracer concentration, and all models simulate unrealistic periods of constant tracer concentration. Recessions in the chloride concentrations are also too rapid in some cases (e.g., 1997–1998). These weaknesses are caused by limitations in all the structures tested which assume a maximum three flow pathways, often decreasing to one flow pathway during recession periods when surface and subsurface stormflow pathways are not active. The short-duration fluctuations are largest in the Topmodel architecture because water ages differ most strongly between the upper and lower reservoirs, the same characteristic which produces realistic extended recession curves. In reality, chloride concentrations represent an aggregation of pathways derived from the spatial and temporal heterogeneity of the catchment [as shown by *Rinaldo et al.*, 2006]. This aggregated solute mixing behavior is analogous to that found for flow recessions at the catchment scale which integrate the behavior of many hillslopes [*Harman et al.*, 2009].

### 4.2. Model Structure Evaluation: Mean Transit Times

[33] In this section we investigate the effect of model structure on MTT and compare the six FUSE model estimates of MTT with those previously derived for the Loch Ard B10 catchment. The MTTs predicted by the FUSE models are all relatively short, less than 150 days (Figure 7). There is a marked split whereby models which use a single upper state variable (S/1Linear, S/2Linear, S/Topmodel) have longer MTTs than those which use split upper state variables for tension and free storage (Sp/1Linear, Sp/2Linear, Sp/Topmodel); resulting from the different mixing characteristics as described in section 4.1. Short MTTs are consistent with the dominant responsive soils (peats, gleys) that generate a quick flow response in the Loch Ard catchment. Indeed, previous work has shown dominant soil cover to be the best single landscape predictor of catchment MTTs in the Scottish Highlands [*Hrachowitz et al.*, 2009a; *Rodgers et al.*, 2005b; *Speed et al.*, 2010; *Tetzlaff et al.*, 2009]. Previous estimates of the MTT (Table 4 and Figure 7) are typically longer than the FUSE estimates, and have a wide range due to the range of models used (refer to Table 4), highlighting the difficulty of choosing an appropriate TTD shape,

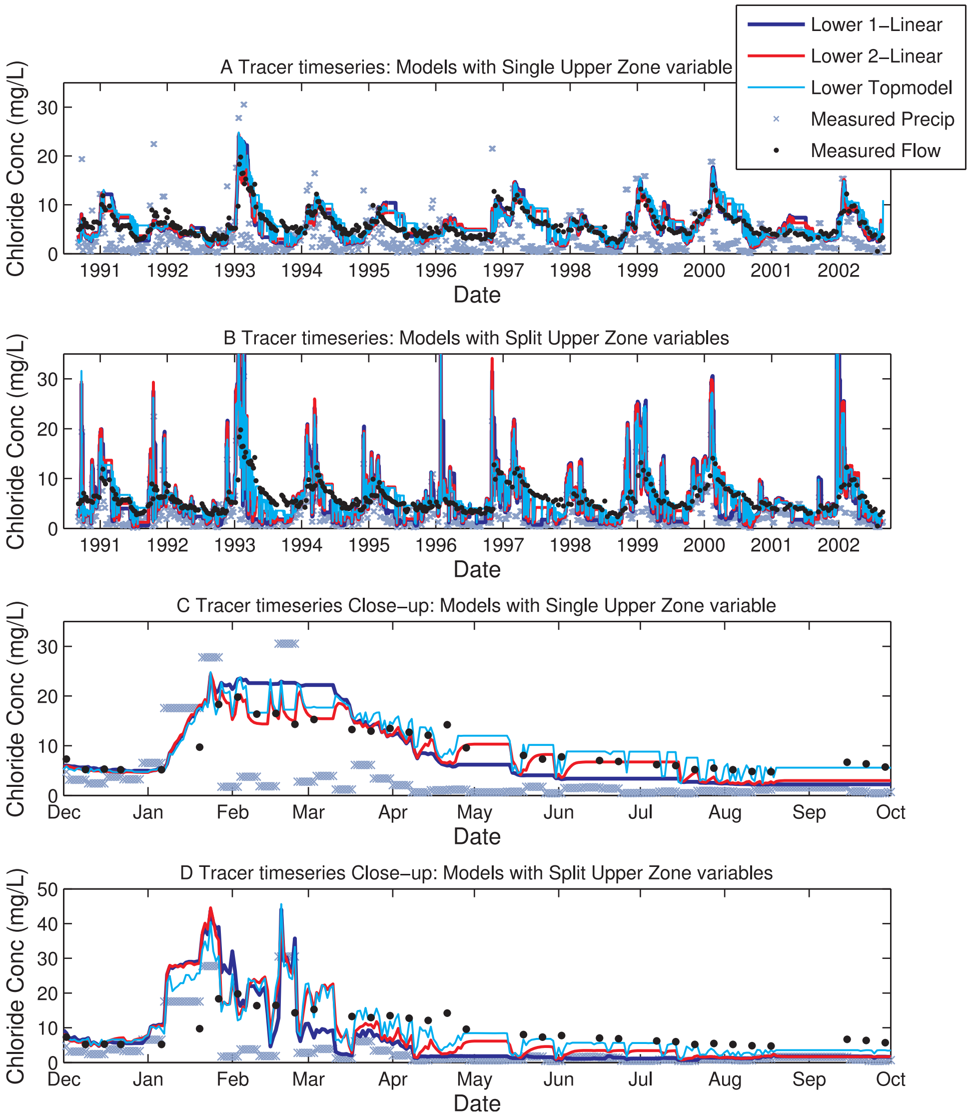


**Figure 6.** Time series of measured chloride input and output concentrations and comparisons with model predictions. (a) Models with a single upper zone storage variable. (b) Models with split upper zone storage variables. (c) Closeup of (a) for largest event (December 1992–October 1993). (d) Closeup of (b) for largest event.

particularly under an assumption of time invariance. The time invariance assumption may also lead to an under-representation of fast flow pathways and hence a longer MTT (refer to section 4.3.2 for a discussion). The FUSE models demonstrate that the range in MTT due to dynamic wetness conditions can be greater than the range due to choice of model structure.

### 4.3. Synthetic Experiments

[34] The FUSE models can be used to investigate the relationship of model structure to simulated water age characteristics. The performance of the models in reproducing tracer concentrations (Figure 6) can then be used to judge which types of water age dynamics are most realistic. The models can be used to investigate aspects of water age which we are not currently able to measure directly, such as TTDs.

#### 4.3.1. Steady State Models

[35] In real conditions, TTDs can change seasonally or by event [*McGuire and McDonnell*, 2010; *Weiler et al.*, 2003] in any catchment due to varying catchment wetness [*Birkel et al.*, 2012; *Hrachowitz et al.*, 2010; *McGuire et al.*, 2007; *Nyberg et al.*, 1999]; this correspondingly causes temporal variation of MTTs [*Lindstrom and Rodhe*, 1992; *Turner et al.*, 1987]. We initially avoided this complexity by using a synthetic constant precipitation input, to determine whether different model structures simulate different steady state water TTDs (even when simulated flow dynamics are similar) and how that gives rise to the different tracer dynamics shown in Figure 6.

[36] Each catchment model was run with constant rainfall and PET input set at the average per time step depth. The models were spun up to steady state (1 year) and then run for a further 11 years to capture the TTD including the

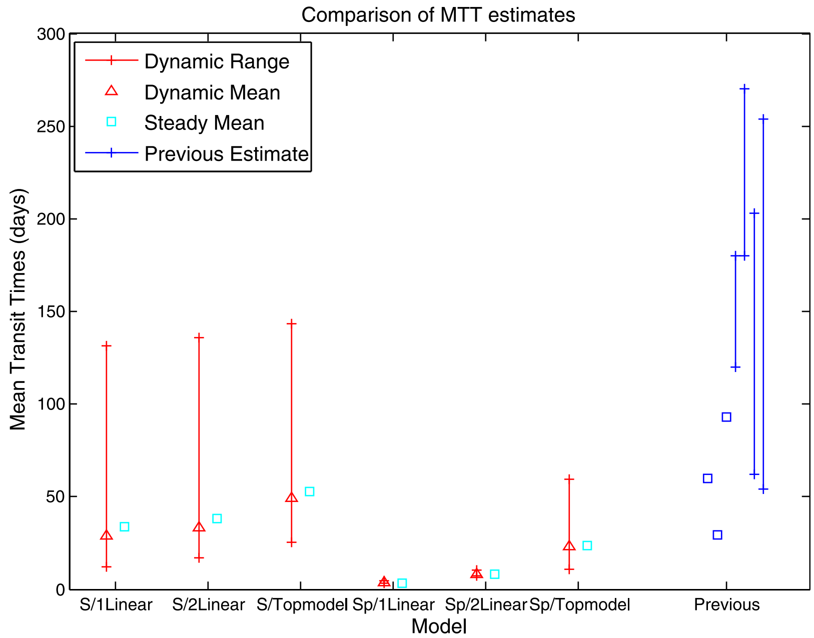


**Figure 7.** Comparisons of MTT estimates between models (run in dynamic and steady state mode) and from previous studies (Table 4) of the B10 catchment.

tail, consistent with the findings of *Hrachowitz et al.* [2011] who found that a spin-up period of approximately 3 times the MTT was required. The steady state TTDs are shown in Figure 8 for (a) total subsurface flow and (b) deep groundwater only.

[37] The TTDs demonstrate clear differences between model structures. The total flow TTDs show that models with split upper state variables have a more peaked initial response than those with a single variable. This helps to explain differences in simulated tracer dynamics, as the former route storm water more quickly to the channel with less mixing with older water. The poorer performance in tracer simulation for these models shows that this is a less realistic conceptualization, concurring with previous studies which highlight the importance of deep flow pathways for solute transport [e.g., *Botter et al.*, 2008].

[38] The maximum of the distribution is typically close to zero indicating the dominance of fast flow pathways; although models using a single upper state variable and linear lower zone reservoirs have a slightly later maximum. Nonzero peaks have been found in previous studies, e.g., *McGuire et al.* [2007] who simulated bromide tracer flux in a steep hillslope with gravelly clay loam soils over relatively low permeability bedrock and found that modeled TTDs peaked at 10 days rather 0 days. In some drier climates, lags may also be related to inter-arrival times of storms or wet periods when more than one storm event is required to flush the tracer through the catchment ([*Rinaldo et al.*, 2011]; the climate example used was 180 mm yr$^{-1}$ rainfall with 10% rainy days). The models using the Topmodel formulation, most successful in simulating tracer response, have flatter responses than those using linear reservoirs. Note that the TTDs given do not include the saturation excess flow pathway: this pathway provides an unmixed pulse of tracers at transit times of <1 day. The TTDs for base flow only (indicative of the behavior of the catchment in a drier state) are flatter with more delayed responses showing the longer transit times for water following deeper flow pathways.

**Table 4.** Previous Estimates of MTT in the Loch Ard B10 Catchment

| Reference | Model | MTT (Days) |
|---|---|---|
| *Tetzlaff et al.* [2007a] | Exponential | 120–180 |
| | Exponential-piston flow | 180–270 |
| | Sine wave | 60 |
| *Godsey et al.* [2010] | Gamma ($\alpha = 0.56$) | 29.2 |
| *Hrachowitz et al.* [2009b] | Exponential | 93 |
| | Gamma | 62–203 |
| | Two parallel linear reservoirs | 54–254 |

#### 4.3.2. Effect of Rainfall Variation and Antecedent Catchment Wetness on Water Transit Time Distribution

[39] Section 4.3.1 examined the case of the catchment in steady state, and hence an invariant transit time distribution. This assumption lies behind the majority of interpretations provided of experimental data for MTTs which use a fixed distribution to model the TTD. In reality, TTDs vary according to the wetness state of the catchment on both a seasonal and event time scale. Recently, the time variant nature of TTDs has been stressed by *Botter et al.* [2010] who also developed the underlying theory. Complementary work by *Hrachowitz et al.* [2010] demonstrated inter-annual variation in gamma TTDs and showed that the *b* (scale) parameter could be linked to precipitation intensity. However, when applied to a catchment like Loch Ard B10, time variance may be weaker due to the year-round wet climate and peaty soils, as has been found in other case

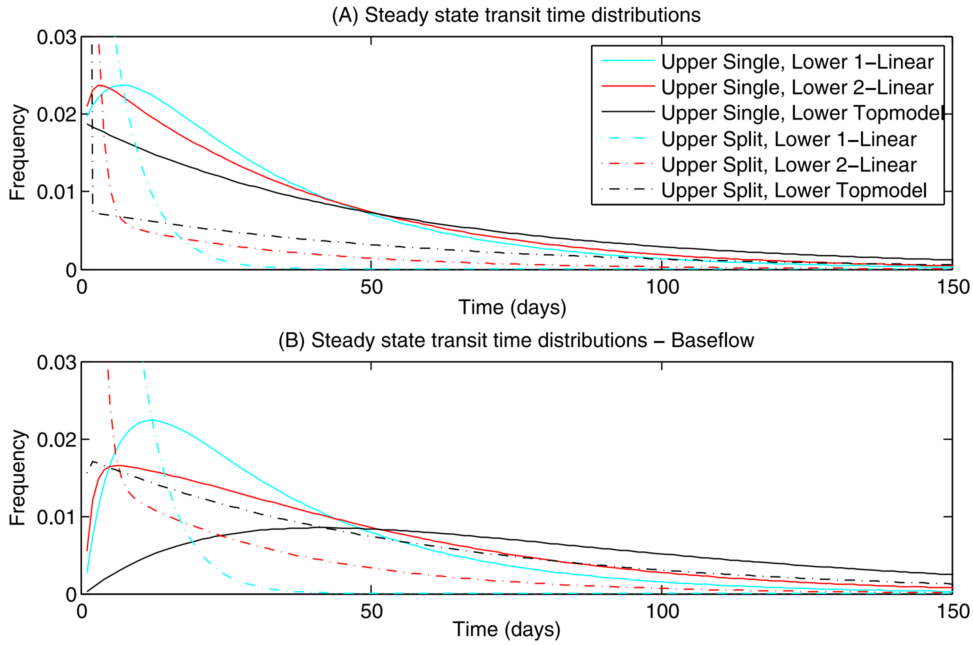


**Figure 8.** Steady state transit time distributions for a range of model structures. (a) Combined flow: subsurface stormflow + groundwater flow. (b) Groundwater flow only.

studies carried out in wet catchments [*Hrachowitz et al.*, 2010; *Rinaldo et al.*, 2011]. The long data record also helps to ensure that the full range of catchment response pathways is captured and hence a stationary TTD more completely represents catchment behavior.

[40] The FUSE framework allows us to explore the TTD time variation simulated by different model structures, and hence test the hypothesis that these variations are required for realistic tracer simulation. Here the FUSE models were driven using the recorded precipitation time series (after spin-up to steady state as for section 4.3.1). Figure 9 demonstrates how MTT varies over a multiyear period, showing strong seasonal variation in four of the six models. The longer MTTs during dry periods contribute proportionately

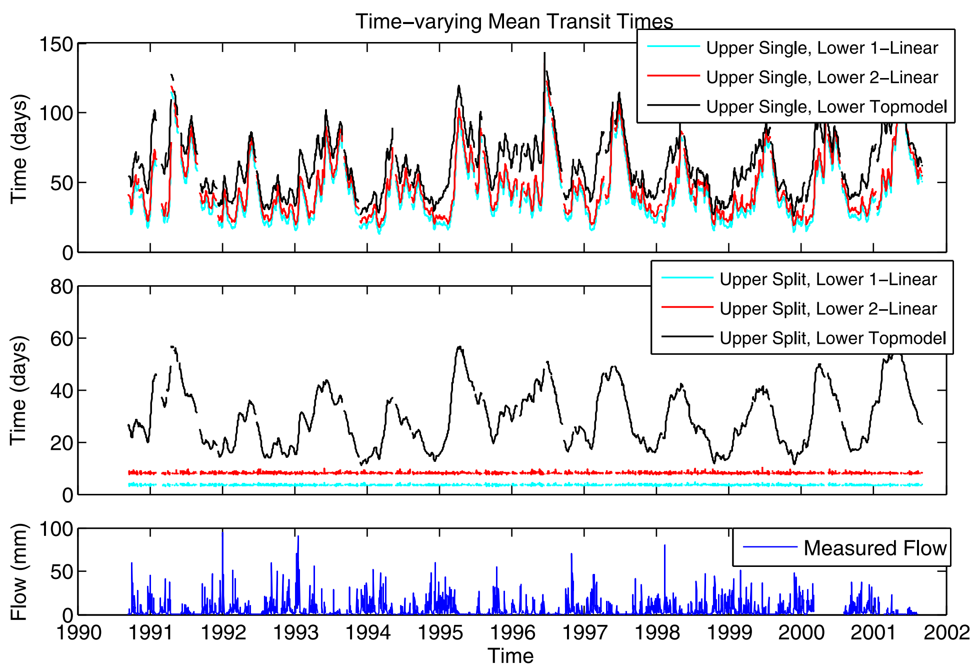


**Figure 9.** Variation of mean transit time with time for a range of model structures (a) Models with single upper state variable. (b) Models with split upper state variables. (c) Measured flow is plotted for comparison.

less to the total MTT due to the weighting effect of the lower fluxes involved. Note that the modeled dry season MTTs are still relatively short, reflecting the small size of the actual groundwater stores at Loch Ard and their rapid turnover. The two models with weak seasonality have split upper state variables and linear lower reservoirs, and display very short MTTs (<10 days) which vary with individual rainfall events rather than the seasonal cycle. Models with a single upper state variable display longer MTTs as these simulate greater mixing of water within the soil zone (a conceptualization of mixing of water held in tension in the soil matrix with free water in the matrix or macropores). The structure of the lower zone also affects MTT: in particular the Topmodel formulation leads to longer MTTs since the nonlinear drainage function means that a greater volume of water is retained in the lower store between rainfall events.

[41] By comparing the MTT variability (Figure 9) with model tracer simulations (Figure 6) we see that the models which simulate longer, seasonally varying MTTs provide most realistic tracer dynamics. However it is not sufficient for a model to reproduce the seasonal cycle in MTT to achieve good performance. For example, the model with split upper state variables, and Topmodel formulation lower architecture, produces a seasonal cycle due to the larger lower store, but produces unrealistic event-scale tracer response due to lack of simulated mixing in the upper soil zone. None of the models tested are able to simulate long MTTs without also producing a seasonal cycle in MTT, because tracers that persist over multiple months are subject to seasonal changes in the model wetness state that are necessary to simulate seasonal differences in the flow dynamics.

[42] In addition to the MTT, the full TTDs for different wetness conditions can be compared with both the master and steady state TTDs (Figure 10). This helps to determine whether steady state models can produce a good approximation to the master TTD. The answer is likely to be catchment specific, as catchments with less pronounced fluctuations in their climate (including seasonality and other time scales) will have more similar master and steady state TTDs. Here we show TTDs for the three model structures which simulated the most realistic tracer series, i.e., upper zone modeled with a single variable, three lower zone architectures. In all cases, there is a strong differential between TTD shapes in wet and dry conditions for fast flow pathways (less than 30 days). In particular, the dry TTD is bimodal with peaks at <5 days and 50–60 days, but a reduction in flow paths compared to the wet TTD in the approximate range 5–30 days. The differences between wet and dry TTDs are due to the initial water depth in the model, the extent to which later rainfall fills model stores and increases flow, and the proportions of runoff from saturation excess flow, interflow, and base flow.

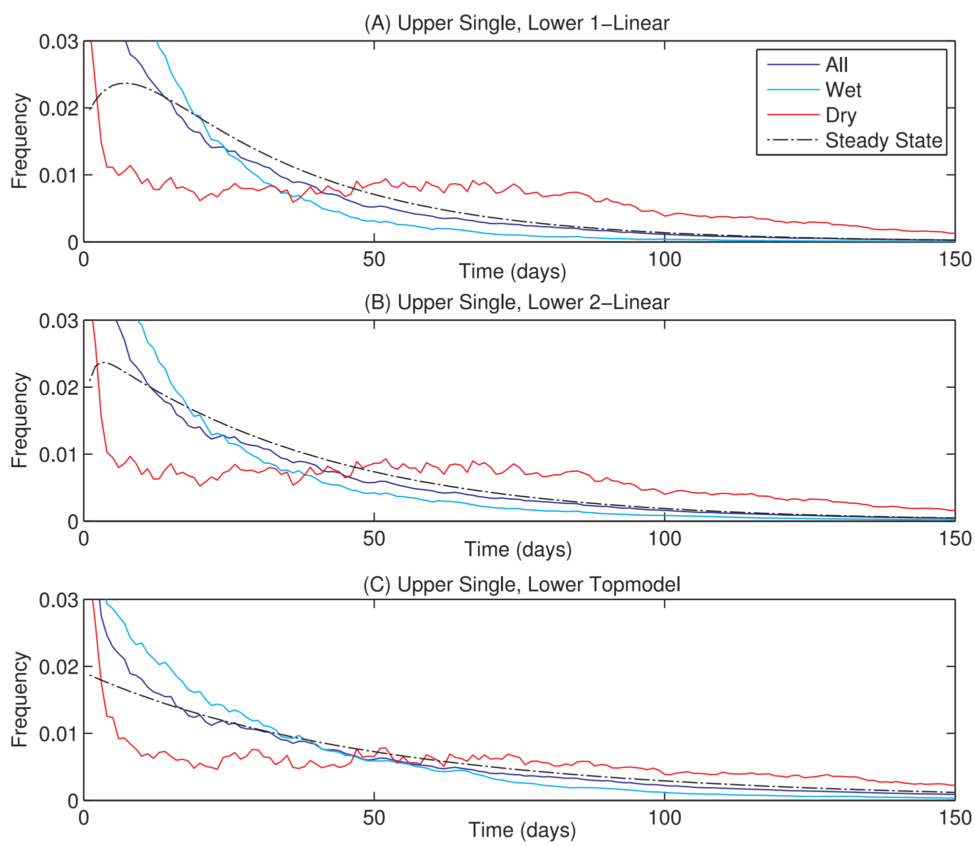


**Figure 10.** Variation in transit time distribution according to catchment wetness condition for three model structures. TTDs are given for (All): all days in record, (Wet): days in lower quartile of MTT distribution, (Dry): days in upper quartile of MTT distribution, (Steady State): steady state TTD for comparison.

[43] The differences in TTD for time scales up to 30 days for wet and dry conditions (with corresponding differences between the master and steady state TTDs), suggest that steady state models will not simulate realistic tracer transport at short time scales. However, at longer time scales there is less difference between TTDs for wet or dry conditions, especially in the best performing model (Topmodel formulation) where all TTDs have heavier tails. We conclude that for slow flow pathways in the B10 catchment, the dynamic nature of the TTD is less important and could reasonably be approximated by a steady state model. In log space (not shown) the steady state TTDs are approximately linear, suggesting that an exponential model could be used. However the dynamic TTDs show additional fast flow pathways which are not captured by the exponential distribution. This helps to explain why a gamma function is often found to be more successful than an exponential function in reproducing tracer dynamics [*Godsey et al.*, 2010], especially at the event scale [*Birkel et al.*, 2012], although modeled TTDs do not always conform to simple statistical distributions [*Dunn et al.*, 2010].

### 4.4. Sensitivity of TTDs to Model Parameters

[44] The model TTD is sensitive to parameter values as well as model structure. Although most parameters were set using field knowledge, there is still uncertainty in the appropriate value at model scale. We therefore undertook a sensitivity analysis to investigate the effect of available depths of upper and lower zone storage on the model TTD, allowing some insights into the interplay of model structure and parameterization. The storage depths were chosen as parameters to be varied because the depth of water available for mixing is known to be an important control on model ability to simulate tracer dynamics [*Fenicia et al.*, 2010].

[45] The model used was [upper zone: single variable, lower zone: Topmodel], as this produced the most realistic simulation of tracer dynamics (Figure 6). The effects of changing upper and lower zone storage depths on TTD and model performance are shown in Figure 11. The results show that the TTD is more sensitive to the size of the upper zone store than the lower zone. We suggest that this is due to the greater nonlinearity of response in the upper store which is controlled by a threshold rather than a power function. The changes resulting from perturbation of upper zone size are of comparable magnitude to those resulting from a change in model structure and should therefore be considered alongside model structure when creating a model which realistically reproduces tracer dynamics.

[46] Figure 11 also shows that model performance is more sensitive to the size of the lower zone store than the upper. Performance falls quickly away from the optimal value. Less sensitivity is found to the size of upper zone store but model performance could be slightly improved by increasing the store size above the value of 320 mm set using results from field knowledge, with a corresponding increase in MTT.

### 4.5. Sensitivity of TTDs to Mixing of Saturation Excess Flow

[47] An important decision in the modeling process was whether saturation excess flow should be treated as mixed

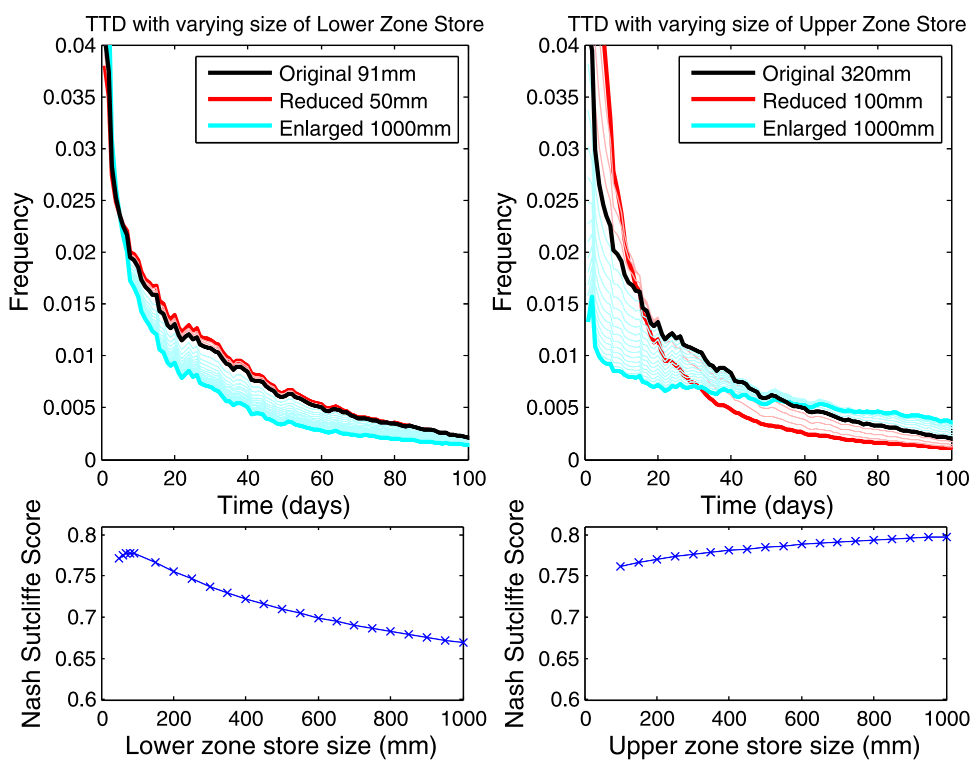


**Figure 11.** The effects of changing upper and lower zone storage depths on transit time distribution (upper panels) and model performance (lower panels). TTDs are shown for equal increments/decrements of store size (thin lines) up to the maximum/minimum values given (thick lines).

or unmixed with subsurface stormflow. In some environments, high intensity rainfall may run off quickly and be missed by weekly sampling. However in the Loch Ard wet environment with peaty soils and relatively low intensity frontal rainfall, there is usually ready availability of water in the upper organic horizons for mixing and hence the displacement of resident soil water becomes the dominant source of runoff.

[48] To explore this question a sensitivity analysis was carried out into the effect of flow partitioning between surface (unmixed) and subsurface (mixed) pathways. We used the model with a single upper state variable and two parallel linear reservoirs, because it provides a good simulation of tracer dynamics during high flows (when surface pathways are active) and the effect of surface flow mixing can be easily studied by changing the parameter "ARNO/VIC *b* exponent" which controls the quantity of surface versus subsurface flow by changing the estimate of saturated area based on upper zone soil water storage (see model equation in Table 1). The results (Figure 12) show that the TTDs are relatively insensitive to the introduction of additional water into the soil zone (i.e., increasing *b*), when compared to sensitivity to store sizes (Figure 11). We therefore suggest that in this case it is acceptable to make the simplifying assumption the saturation excess flow is unmixed.

## 5. Discussion

[49] Water transit time characteristics provide a valuable diagnostic tool for evaluation of model structure, to complement the traditional comparison of modeled and measured discharge series, as shown both in this and previous papers [*Birkel et al.*, 2011b]. While other data sources such as soil moisture or depth to water table can also be used for multiresponse evaluation, they are typically point measurements subject to the "scaling problem" [*Blöschl and Sivapalan*, 1995; *Sivapalan et al.*, 2004]. Tracer dynamics are particularly useful as they provide an alternative integrated signal to the hydrograph.

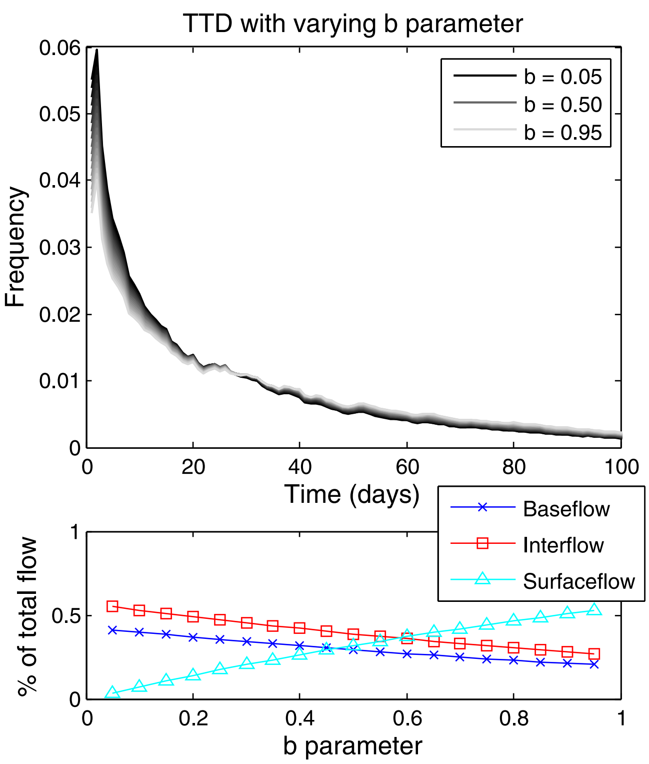


**Figure 12.** The sensitivity of the model to soil water mixing is shown by varying the surface flow *b* parameter. Effects are shown on transit time distribution (upper panel) and percentage share of flow volume between pathways (lower panel).

[50] In return, hydrological models (including mixing assumptions) provide a tool for investigating scenarios of water TTD shape, and variability with catchment wetness. These characteristics are not directly measurable using environmental tracers, and hence models provide a method for their estimation. An estimate of the TTD shape is required for studies which use inverse modeling to obtain MTT estimates and then apply the results to simulate tracer, chemical, or contaminant transport [*McDonnell et al.*, 2010]. It is hoped that future work will indicate whether distribution shapes and variability are transferable between neighboring or hydrologically similar catchments.

[51] This study relied on several assumptions. First, uncertainty in rainfall, climate, streamflow, and chloride measurements was not considered, although it is well known that measured hydrological data is subject to many sources of uncertainty [e.g., *Andreassian et al.*, 2004; *Beck*, 1987; *Pelletier*, 1988]. These uncertainties can have substantial effects on calibrated parameter values [e.g., *McMillan et al.*, 2010] and may therefore indirectly affect water transit time characteristics predicted by the model. A second assumption was that the effects of dry deposition and biogeochemical cycling on chloride concentrations were modeled using a constant, multiplicative adjustment factor to correct the mass balance (refer to section 2.3).

[52] Our modeled transit times were generally shorter than previous estimates from tracer data, consistent with previous findings that model storage volumes required to capture water quantity dynamics are smaller than those required to reproduce tracer dynamics [e.g., *Fenicia et al.*, 2010]. Our work highlighted the value of FUSE to understand which model structure and TTD characteristics (shape, time variability) enable simulation of both flow and tracer concentrations. For example, at Loch Ard this could be achieved using a Topmodel style nonlinear lower zone store, with a TTD which has a greater weight of fast flow pathways than the exponential distribution and varies with catchment wetness at short time scales. Although previous studies have shown that water and tracer dynamics can be used to tailor a model for an individual catchment [e.g., *Birkel et al.*, 2011b], the FUSE framework provides much greater flexibility in model structure. It leads toward a robust, transferable method for water and tracer modeling that could be relatively easily used in a wide range of catchments by selection of appropriate FUSE model components according to process knowledge or structural diagnostics, on a per catchment basis or using a regionalization method.

[53] The study has also led to recommendations for model structure options that could be added to FUSE to improve the concurrent representation of streamflow and tracer dynamics. For example, subsurface stormflow is currently modeled as a linear function of free storage in the

upper zone. When this pathway is used in a model with separate state variables for tension and free storage, the free storage becomes a very fast response store with low transit times. Recent ecohydrologic experiments suggest that in a strongly seasonal, Mediterranean climate where there is significant summer soil drying, water in the soil matrix may be largely decoupled from that in fast flows paths [*Brooks et al.*, 2010; *Phillips*, 2010]. In climates where it occurs, this behavior would be more closely modeled by the split upper state variables approach. One method to reconcile longer mean transit times with split state variables would be to use a nonlinear response function for interflow (e.g., a power function similar to those used to model percolation).

[54] There are many needs for future research into transit time distribution characterization; a summary was provided by *McDonnell et al.* [2010]. This study highlighted that although MTT provides a very useful summary statistic of catchment behavior, there is a need for better measurement techniques which work toward characterization of the complete time-variable TTD: this would reduce ambiguity in transit time estimates and provide extremely valuable data against which to test different model structures. Furthermore, although of lesser importance in a fast-responding catchment such as Loch Ard, conservative/natural tracers are not adequate to capture behavior in catchments with MTT of greater than a few years [*Hrachowitz et al.*, 2009a; *Stewart et al.*, 2010], meaning that alternative tracers or methods are needed to investigate TTD tails in catchments with long response times. Improved understanding of the true TTD would also help to counter other causes of bias such as stream water tracer sampling biased toward low flows, or model inability to differentiate multiple deep groundwater stores.

## 6. Conclusions

[55] In this paper we demonstrated how augmenting the FUSE rainfall-runoff modeling framework with a water-tracking ability provides the opportunity to use tracer data as an additional model structure diagnostic. Using a range of calibrated models for the Loch Ard B10 catchment in Scotland, we showed that different model structures which provide very similar flow dynamics (and hence performance as measured by a sum-of-squared-errors score) can produce very different simulations of water TTD and tracer dynamics. We evaluated different model structures against streamflow tracer dynamics using weekly observations of tracer concentration. In the Loch Ard catchment, a model structure could be selected to provide good simulations of both flow and tracer dynamics. We used the water-tracking models as a hypothesis testing tool to explore the effect of catchment transit time characteristics on model behavior and performance. Across model structures we showed strong seasonality and event-scale fluctuation in MTT and TTDs; and corresponding differences between dynamic and steady state TTDs. The results suggest that steady state approximations to the catchment TTD at Loch Ard will not simulate realistic tracer transport at short time scales (<30 days), although differences are less marked at longer time scales. The FUSE framework with water age characterization provides a tool to investigate flow and tracer modeling in competing model structures, which could be relatively easily applied to many catchments.

[56] **Acknowledgments.** The authors are grateful to Iain Malcolm of Marine Science Scotland's Freshwater Laboratory for access to the Loch Ard chloride data. We thank Tobias Krueger and two anonymous referees for their thorough and constructive reviews.

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M. Clark, National Center for Atmospheric Research, PO Box 3000, Boulder, CO 80307-3000, USA.
H. McMillan, National Institute of Water and Atmospheric Research, PO Box 8602, Christchurch 8440, New Zealand. (h.mcmillan@niwa.co.nz)
D. Tetzlaff and C. Soulsby, Northern Rivers Institute, School of Geosciences, University of Aberdeen, Aberdeen AB24 3UF, UK.