# Factors influencing the residence time of catchment waters: A virtual experiment approach

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[1] Estimates of mean residence time (MRT) are increasingly used as simple summary descriptors of the hydrological processes involving storage and mixing of water within catchment systems. Current understanding of the physical controls on MRT remains limited, and various hypotheses have been proposed to explain its variability between catchments. We present a series of virtual experiments to investigate different hypotheses regarding the significance of different hydrological processes and geographical controls in determining the MRT of catchment waters. The experiments were undertaken using a semidistributed conceptual hydrological model, applied to the Maimai experimental catchment in New Zealand. Our results show that in this small steep catchment, with largely impermeable bedrock, the primary control on the stream water mean residence time is storage within the unsaturated zone. The physical location on the hillslope had only a small influence on soil water residence time. Stream water mean residence time was very sensitive to small additional amounts of deep groundwater in the model. Overall, our results suggest that stream water MRT is additive. The component residence times of stream water MRT appear relatable to characteristic properties of the catchment. Through this mechanism there is future potential for extrapolating MRT data from experimental catchments to other areas.

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## 1. Introduction

[2] The use of hydrochemical and isotopic tracers to infer hydrological processes has become increasingly common in catchment hydrological studies (for reviews see *Kendall and McDonnell* [1998] and *Divine and McDonnell* [2005]). Unlike point-scale hydrometric observations, tracer techniques provide a means of obtaining spatially integrated information about catchment mixing that is relevant at all scales [*Soulsby et al.*, 2000]. These data often provide complementary information to traditional flow measures at the catchment outlet for quantifying water flow paths [*Bishop et al.*, 2004] and water sources [*Burns*, 2002]. One particular catchment measure that is sometimes estimated from tracer data is the stream water mean residence time (MRT) [*Maloszewski and Zuber*, 1993]. MRT, sometimes defined as transit time [*McGuire and McDonnell*, 2006], or contact time in the subsurface [*Burns et al.*, 1998], is the mean of the complete distribution of flow paths comprising the catchment subsurface control volume. The stream water (or catchment) MRT provides a simple descriptor of the effects of storage and mixing within the catchment in terms of its temporal response to precipitation inputs. Furthermore, the residence time distribution or system response function provides a concise expression of flow path heterogeneity at the catchment scale. In the context of this paper we use the term "catchment MRT" as the general term for the collection of component residence times, that are described by soil water MRT, groundwater MRT and in-stream MRT.

[3] While recent experimental studies have developed new quantitative approaches for computing stream water MRT from tracer data [*Kirchner et al.*, 2000] and evaluated the assumptions associated with its calculation from traditional tracer approaches [*McGuire and McDonnell*, 2006], few studies have examined how catchment characteristics control MRT. The lack of studies is due partly to the extreme field time demands and analytical costs of computing MRT, since many years and many hundreds of samples are required for analysis. As a result, the total number of studies that have reported MRT is small. MRT values for stream waters in small headwater catchments have ranged from a few months [*Stewart and McDonnell*, 1991] up to almost two years [*Burns et al.*, 1998], but with an estimated MRT of groundwaters in some catchments greater than ten years [*Rademacher et al.*, 2005; *Reddy et al.*, 2006]. For large river basins, many studies report river MRT on the order of a decade [*Michel*, 1992]. Most studies to date have been designed to compute MRT of catchment soil water, groundwater and stream water at a particular site.

[4] While studies are few, some hypotheses have been advanced to explain the catchment controls on MRT of stream waters. *DeWalle et al.* [1997] and *Wolock et al.*

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[1997] have suggested that MRT may be correlated with catchment size, using the argument that greater groundwater storage and mixing occurs in larger catchments because of longer flow paths for subsurface flow, together with shallower gradients in wider valley floors. Other studies have suggested that topography controls stream MRT. *Stewart and McDonnell* [1991] and *Rodhe et al.* [1996] found that MRT of soil waters increased down a hillslope with increasing flow length. This hypothesis was later rejected by *Asano et al.* [2002] for catchments with permeable bedrock where there was no evidence for downslope water ageing. *Buttle et al.* [2001] also examined the influence of topography on groundwater residence times by searching for an association between the ln ($a$/tan $\beta$) topographic index and residence time. No strong relationship was found between the values, suggesting that in their catchments, topography was not the key driver of MRT. However, groundwater residence times were found to increase with proximity to the stream [*Monteith et al.*, 2006]. Recently, *McGlynn et al.* [2004] and *McGuire et al.* [2005] presented data across multiple nested catchment scales and found a positive correlation between catchment MRT and both the flow length and the flow path gradient derived from a catchment digital elevation model (DEM). A further group of studies have examined the relationship between the catchment MRT and the distribution of soil types within a catchment [*Rodgers et al.*, 2005; *Soulsby et al.*, 2006]. In particular, *Soulsby et al.* [2006] identified relationships between the percentage of freely draining soils and the percentage of peaty soils and the catchment MRT. These results indicated a quite different set of controlling processes on the MRT to those linking MRT to topography.

[5] The integrative nature of MRT, capturing the response of catchments including heterogeneity, suggests that it may prove to be a useful measurement from the standpoint of model evaluation. *Uhlenbrook and Leibundgut* [2002] and more recently *Vaché and McDonnell* [2006] and others have begun to investigate its use as a catchment model diagnostic and model evaluation tool. The fact that MRT probes an alternative axis of catchment response to that revealed through the standard catchment hydrograph (namely particle transport as opposed to pressure wave propagation) means that it is a useful tool for discriminating catchment storage and mixing processes. In this paper, we argue that examination of the physical controls on MRT is a critical next step in catchment hydrology and precondition for its continued use as a model diagnostic. While intercomparison of existing MRT data from catchments around the world would be the best way to start [*Jones and Swanson*, 2001], there are unfortunately, insufficient data sets available for inter watershed comparison and analysis of the factors affecting stream MRT. Therefore we have developed a novel methodology, based on the virtual experiment approach of *Weiler and McDonnell* [2004], to examine how the catchment MRT disaggregates into different components for each process occurring in the catchment. We define the virtual experiments as numerical experiments driven by knowledge of field behavior, and the mathematical model is used as a learning tool for understanding the MRT phenomenon. Thus, from the results of the experiments, we can develop hypotheses about how catchment topography, geology and soil drainage processes influence the catchment MRT.

[6] The main objective of this paper is to investigate different hypotheses regarding the significance of hydrological processes and geographical controls in determining the MRT of water within a catchment. Specifically we explore how soil porosity, unsaturated zone processes, flow path length and gradient, deep groundwater storage and riparian zone storage each affect computed stream water MRT. The well studied Maimai catchment in New Zealand is used as our case study, with a rich history of research providing appropriate field intelligence about hydrological processes and residence times (see *McGlynn et al.* [2002] for review).

## 2. Experimental Approach

[7] The basis of the experimental approach for the study was to use a conceptual hydrological model to run a series of simulations designed to test how different physical factors could influence the residence time distributions of water in a catchment. The structure of the model code enabled several different formulations of the model to be executed, by including and excluding different processes from the simulations. In this way it was possible to test the sensitivity of the modeled residence times to particular model components. In addition, topographic influences could be tested through simple manipulation of the underpinning digital terrain model.

### 2.1. Model Code

[8] A new model code, STorage REsidence times And Mixing in catchments (STREAM), was developed for the analysis, based on two previous semidistributed conceptual models: DIY [*Dunn et al.*, 1998] and NIRAMS [*Dunn et al.*, 2004]. The STREAM model is coded in VB.net and loosely linked to a GIS via ArcGIS ascii grid input/output files. The catchment is represented in STREAM by a grid of square cells, typically of 10–50 m in size, each of which is characterized by a range of properties including elevation, soil type and several topographic descriptors. The topographic descriptors define how the hydrology of each cell is linked with the remainder of the catchment, as well as the routing of flows from the land to the stream.

[9] For each grid cell, effective precipitation (rainfall minus evapotranspiration) is added to a soil store, where a water balance is calculated at each time step. A fraction of the soil water drains to both a near surface and subsurface store, at a rate dependent on the soil water store. If the soil is fully saturated, direct surface runoff also occurs. The full set of equations for the soil water balance is detailed by *Dunn et al.* [2004]. The water balance equation for the soil store is

$$SS_{i,t} = SS_{i,t-1} + P_{i,t} - DNS_{i,t-1} - DG_{i,t-1} - EX_{i,t-1} \qquad (1)$$

where $SS_{i,t}$ is the soil storage for cell $i$ at time $t$ (m), $P_{i,t}$ is the net precipitation (precipitation minus evapotranspiration) (m), $DNS$ is the drainage to the near surface store (m), $DG$ is the drainage to the shallow groundwater (m) and $EX$ is the loss by saturation excess surface runoff (m).

[10] Water from both surface runoff ($EX$) and the near surface store ($DNS$) is assumed to flow directly to the stream network, via macropores, rills and small channels,

at a rate that is sufficiently rapid to neglect the detailed routing of the flow down the hillslope.

[11] Water from the subsurface store of each grid cell generates shallow groundwater flow. The flow is routed to a surface stream via a series of hillslope cells, defined according to the topographic location of the grid cell. The simulation for each individual grid cell can be performed independently of all other cells in the catchment, as the routing function for each cell is disaggregated from neighboring cells. The approach is very similar to that applied within the DIY model [*Dunn et al.*, 1998] except that within STREAM the routing equation includes a weighting factor to account for the position of each hillslope routing cell in relation to the remainder of the catchment. The shallow groundwater flow is defined by:

$$QG_{i,t} = KG \times GS_{i,t} \times SlD_i \times W \times F_i \tag{2}$$

where $QG_{i,t}$ is the flow for cell $i$ at time $t$ ($m^3\ s^{-1}$), $KG$ is the shallow groundwater rate parameter ($m\ s^{-1}$), $GS_{i,t}$ is the subsurface store, $SlD_i$ is the slope from cell i to the stream via its flow path (m/m), $W$ is the dimension of the cell (m) and $F$ is a topographic weighting factor.

[12] $GS$ is calculated for each routing cell by

$$GS_{i,t} = GS_{t-1} + \left(QG_{i-1,t-1} - QG_{i,t-1}\right) \times \Delta t / W^2 \tag{3}$$

[13] $F$ is defined for each cell $i$ by

$$F_i = \frac{SlD_i}{(SlD_i + (SlU_i \times UA_i))} \tag{4}$$

[14] The variable $F$ accounts for the influence of topographic location in modifying the dynamics between the flow rate, $QG$, and the shallow groundwater storage, $GS$. Greater upslope contributing areas will lead to greater storage in the cell. However, the discharge rate depends on the tradeoff between the slope uphill of the cell ($SlU$), and that downhill of the cell ($SlD$) as well as the storage. If $SlU$ is large relative to $SlD$, then the cell will tend to accumulate greater storage than if the reverse scenario is true. Where there is a uniform gradient, the only influencing topographic factor becomes the upslope contributing area (or number of cells), $UA$ (-). The initial conditions for $GS$ are calculated to account for these dynamics by weighting the storage by $1/F$. This gives greater storage of water within the cells with low values of $F$.

[15] The shallow groundwater flow is routed through the appropriate number of cells to correspond to its physical location in the catchment, relative to the stream network. Thus the transport occurs over a lateral distance equivalent to the flow length from each cell to the stream. The flow calculated for the final hillslope routing cell in each case is assumed to be the discharge to the stream cell (or riparian cell if a riparian storage is included in the model).

[16] An optional additional deep groundwater flow has been included in the STREAM model to represent a flow path mechanism that is insensitive to short-term variability in soil moisture. This is produced by a steady uniform recharge from the soil storage to a deep groundwater store. The deep groundwater is then routed down a simplified hillslope (defined for each cell by the mean slope to the stream, and the flow length to the stream). The deep groundwater is not routed through intermediate cells in the same manner as the shallow flows, as it is considered to be much less variable both spatially and temporally. The deep groundwater recharge rate is estimated from the streamflow hydrograph for the catchment as the lowest measured flow rate, assumed to be evenly distributed across the catchment.

[17] Finally, in order to investigate the potential influence of riparian storage on catchment responses, another optional component has been included in STREAM. This defines an additional storage, adjacent to the stream, through which all flows can be routed. The riparian store can be assigned a variable width, depending on the size of the streams, and has a variable depth determined by the soil depth. Flows from the riparian storage are assumed to discharge directly to the streams.

[18] The total catchment streamflow is calculated either by summation of the flows from each riparian cell to the stream, or else by summation of the routed flows originating from each cell in the catchment (when riparian cells are not modeled). In-stream routing of flows within the catchment is not included in the model.

[19] A set of equations defining the transport of a conservative solute tracer are associated with each of the flow equations. The tracer is assumed to be fully mixed within each of the stores through which it passes. An optional effective porosity term is also included to account for the potential influence of immobile water on tracer movement. The inclusion of an effective porosity value (between 0 and 1) means that the transport of the tracer is associated with only a portion of the total available porosity, which effectively disaggregates its response from the discharge response. A mechanism of this type has been observed in unsaturated transport for a wide range of soils, although reported proportions of immobile water are quite variable. *Lindgren et al.* [2004] and *Destouni et al.* [1994] calculated typical values of 2:1 for the ratio of immobile water to mobile water from both experimental and modeling studies. *Buttle and Sami* [1990] found somewhat lower values, with the immobile water accounting for up to 19% of the total volume. For each modeled flow the associated flux of tracer, $TF$ (kg), is defined by

$$TF = \frac{TS \times Q \times \Delta t \times EP}{S \times W^2} \tag{5}$$

where $TS$ is the mass of tracer stored in the compartment (kg), $Q$ is the water flow for a particular model component ($m^3\ s^{-1}$), $\Delta t$ is the time step (s), $EP$ is the effective porosity for transport through the compartment (-), $S$ is the depth of water stored in the compartment (m) and $W$ is the size of the compartment (m). This form of equation applies to the fluxes from the soil storage, the shallow subsurface flow, the near surface flow, the deep groundwater storage and the riparian storage, although in many cases the value of $EP$ will be assumed to be equal to one.

[20] There are a total of 14 potential parameters of the model, depending on which particular components are implemented. The parameters are summarized in Table 1, together with details of how the parameters are determined.

**Table 1.** Parameters of the STREAM Model

| Variable | Units | Description | Model Component | Identification Methodology |
|---|---|---|---|---|
| FC | m | soil field capacity | soil water balance | based on physical data |
| SC | m | soil saturated capacity | soil water balance | based on physical data |
| $\varphi$ | % | soil porosity | soil water balance | based on physical data |
| CV | $s^{-1}$ | subsurface drainage parameter | soil water balance | calibration including data on flow path proportions |
| CL | $s^{-1}$ | bypass flow loss parameter | soil water balance | calibration including data on flow path proportions |
| EP Uz | % | effective porosity | soil water balance | calibration including MRT |
| KS | m $s^{-1}$ | near-surface rate parameter | near-surface flow routing | calibration including high-streamflow response |
| KG | m $s^{-1}$ | shallow groundwater rate parameter | groundwater hillslope routing | calibration using streamflow response |
| EP Gw | % | effective porosity | shallow groundwater flow | calibration including MRT |
| R | m $s^{-1}$ | recharge rate of deep groundwater | deep groundwater | estimation from stream base flow |
| DGI | m | initial depth of deep groundwater store | deep groundwater | estimation in conjunction with dGwK from base flow |
| KDG | m $s^{-1}$ | groundwater conductivity | deep groundwater | estimation in conjunction with dGwsInit from base flow |
| RW | m | width of riparian zone | riparian | based on catchment topography |
| KR | m $s^{-1}$ | riparian rate parameter | riparian | calibration |

Some of the parameters are based on experimental data, others are derived from observed hydrological characteristics of the catchment, and some are based solely on the model calibration. In theory some of the parameters could take spatially varying values (e.g., to represent soil variability). However, where calibration is required and few spatial validation data are available, there is little sense in implementing this because it would increase the degrees of freedom within the calibration procedure, without any physical justification.

[21] The model calibration is undertaken in stages. Initially, where possible, values for the water balance drainage parameters *CV* and *CL* are evaluated to give an appropriate split between the proportion of surface/near surface and groundwater flows. Such data may be available from an end-member mixing analysis [*Soulsby and Dunn*, 2003; *Dunn et al.*, 2006]. Following this, other flow parameters are calibrated using the historic discharge record for the catchment. As demonstrated by many previous studies [e.g., *Beven and Binley*, 1992; *Freer et al.*, 1996] there is an issue regarding equifinality of possible model parameterizations. However, utilization of the catchment MRT can potentially be used as a means of constraining the resulting parameter values [*Vaché and McDonnell*, 2006]. In the context of this study, the absolute parameterization of the model was less of an issue than the exploration of the influences on the prediction of catchment MRT.

## 2.2. Study Area

[22] The study area for the modeling experiments was the Maimai (M8) catchment in New Zealand. The Maimai group of catchments has been the site of experimental field studies since the 1970s including studies focused on residence time calculation and tracer tests on flow path and flow source [*McDonnell et al.*, 1991; *Stewart and McDonnell*, 1991]. The M8 catchment was selected for this study largely because of its history of research, which means that understanding of the processes operating in the catchment is well developed and residence time data are available as well as streamflows. In addition, the physical characteristics and hydrological behavior of the catchment are comparatively simple and spatially homogeneous.

[23] The physical characteristics of the Maimai catchments have been described by *Pearce et al.* [1986] and *McDonnell* [1990]. The M8 catchment covers an area of 3.9 ha, and is steep, wet and highly responsive. The mean slope of the M8 catchment is 34°, with a relatively short hillslope length of around 30 m. The soils are relatively shallow (0.2–1.8 m) and consist of podsolized stony yellow-brown earths, overlain by a well-developed thick humic horizon. The catchment is underlain by a firmly compacted, moderately weathered early Pleistocene conglomerate, which is considered to be largely impermeable [*Mosley*, 1979]. There is a vegetation cover of mixed evergreen forest. The annual average precipitation is around 2600 mm, of which approximately 1550 mm forms stream runoff.

[24] The principal flow process in the Maimai M8 catchment is believed to be subsurface hillslope runoff. During low-flow conditions, slow continual downslope drainage sustains streamflows, with water from upslope areas mixing with and displacing downslope soil water. This mechanism results in a progressive ageing of water downslope [*Stewart and McDonnell*, 1991]. During high-flow events the subsurface flows are supplemented by the development of highly transient macropore-driven processes which rapidly deliver large volumes of previously stored water to first-order stream bank zones [*McDonnell*, 1990]. The impermeable nature of the bedrock means that only a small percentage of the catchment runoff is believed to be sourced from deeper groundwater.

[25] Measurements of $\delta^{18}O$ in the stream and rainwater have been used to estimate a MRT for Maimai of 4 ± 1 month [*Pearce et al.*, 1986]. This is considered to be a relatively short residence time when compared to other catchments, but it is not surprising given the steep and responsive nature of the area and largely impermeable underlying bedrock. Results from a different tracer experiment, based on deuterium analysis, calculated mean residence times for soil water in a number of locations around the M8 catchment ranging from 13 days for shallow soils on midslope locations, to 42 days for soil at 400 mm depth on midslopes and 63 days for soil at 800 mm depth near the stream [*Stewart and McDonnell*, 1991].

[26] These results from previous experimentation provided a set of baseline understanding and data for the modeling experiments carried out in this study.

## 2.3. Virtual Experiments

[27] Prior to execution of the model experiments, a baseline hydrological model of the Maimai catchment was set up and calibrated to provide a believable representation of the catchment hydrology, based on the historical analysis

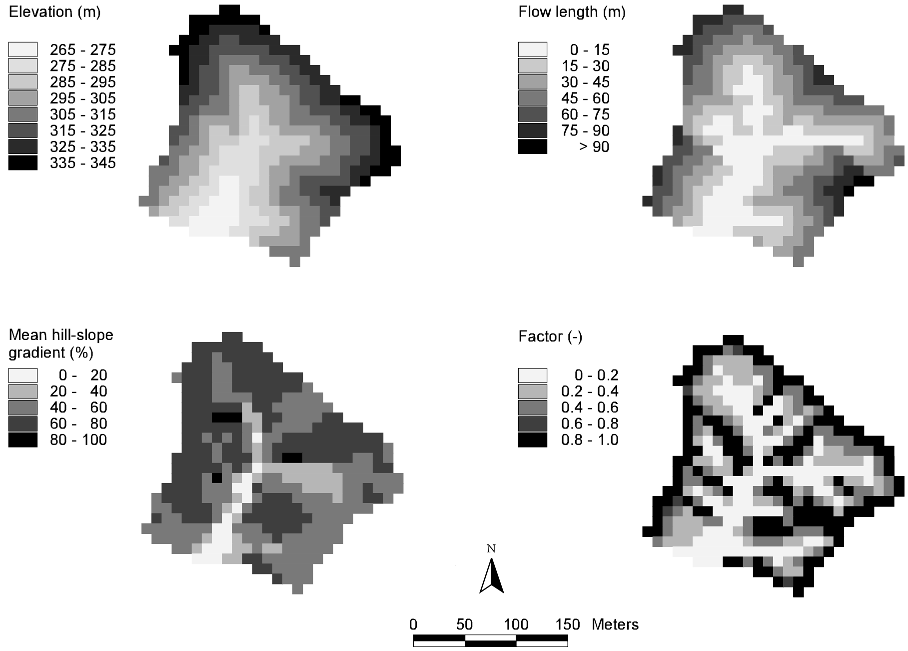


**Figure 1.** Spatial data used for baseline model of the Maimai catchment.

of hydrological processes described above. Simulations were based on a four month period in 1989 when experimental studies were undertaken that involved the collection of deuterium data as well as streamflow and meteorological data [*Stewart and McDonnell*, 1991]. The streamflow data were used to calibrate the model, together with the estimated catchment MRT of four months. Evapotranspiration was estimated a priori from meteorological data using the same method as *Vaché and McDonnell* [2006]. The baseline model of the Maimai catchment was constructed from a 10 m DEM, setting a grid cell size of 10 m. Some of the spatial data sets used for the baseline model are shown in Figure 1. The stream network was derived from the DEM by GIS analysis, with a threshold for flow accumulation set to generate a comparable stream length to that observed on the ground.

[28] A two flow path system was invoked in the STREAM model to correspond with the principal observed flow mechanisms in the catchment. The hillslope runoff was represented by shallow groundwater flow in the model and the rapid highly transient runoff component (or bypass flow) was represented by the combined surface and near surface runoff. Deep groundwater recharge was assumed to be negligible. Drainage from the soil water store (representing the unsaturated zone) was calibrated using the drainage parameters, *CV* and *CL*, to generate an approximate distribution between the two flow components of 60–80% hillslope runoff: 20–40% bypass flow. This corresponds with current expert opinion of the catchment processes based on the historical experimentation. The optional riparian storage was excluded from the baseline STREAM model, as the streams within the Maimai catchment are deeply incised [*Pearce et al.*, 1986] and have minimal riparian zone.

[29] In order to evaluate the MRT of the model a pulse input of tracer was applied uniformly to all cells in the catchment model four weeks after the start of the simulation. The residence time of the tracer in the catchment was calculated from the tracer output flux, *TF*, by

$$MRT = \frac{\int_0^\infty t \cdot TFdt}{\int_0^\infty TFdt} \tag{6}$$

[30] In order to achieve full tracer recovery, the meteorological data were cycled repeatedly and the length of the simulation extended as required. The full model was calibrated using both the measured streamflows and the previous field estimate of MRT.

[31] This model of the catchment was used as a baseline against which a series of six model experiments could be compared. These experiments were designed to test a range of hypotheses regarding controls on the mean residence time of water in catchments and are detailed below. For each experiment the residence times of various components were calculated using equation (6) with the appropriate modeled fluxes of tracer for each process.

#### 2.3.1. Hillslope Flow Processes

[32] Previous interpretation of flow processes in the Maimai catchment has suggested that hillslope flow contributes a significant proportion of the total runoff to streams [*Pearce et al.*, 1986]. This factor combined with observed apparent ageing of water down the hillslope [*Stewart and McDonnell*, 1991] suggest that hillslope flow processes may be a significant control on the residence times of water in the catchment. To examine this factor, model simulations were carried out with the unsaturated zone of the Maimai baseline model effectively bypassed. The potential influence of immobile water within the hillslope transport component was also examined by applying an effective porosity term (*EPGw*) to the transport calculations.

### 2.3.2. Unsaturated Zone Processes

[33] Infiltration in the soil profile is largely influenced by a balance between gravitational and capillary forces. The occurrence of more rapid hillslope transport only occurs once soil moisture conditions have reached a critical level where they effectively saturate the soil, or a portion of the soil. Thus there is the potential for quite long residence times of water within the unsaturated zone.

[34] The simplistic representation of the unsaturated zone used in this model provides a means of describing the retention of water within the soil profile, but does not explicitly track its flow. The incorporation of an effective porosity term (*EPUz*) for the transport of the tracer allows for dissociation of the tracer from the movement of water, to represent the dual porosity system.

[35] The relative importance of unsaturated zone processes compared with hillslope flow processes could be assessed from the simulations performed in (2.3.1), compared with the baseline simulations. In addition, with the representation of the unsaturated zone included again, the sensitivity of simulations to the value of the unsaturated zone effective porosity was evaluated.

### 2.3.3. Flow Path Gradient

[36] The role of catchment topography in determining residence times was evaluated through two topographic characteristics; the flow path gradient and the flow path length. The gradient of the hillslope affects the rate of groundwater flow routed down the hillslope. If the storage in the shallow groundwater was an important control in determining the MRT, then it would be expected that the gradient of the slope would have a strong influence on the MRT.

[37] The flow path gradient was examined by comparing model simulations based on the same catchment structure as that of the Maimai catchment, but effectively flattening out the gradients, by dividing the digital elevation model by factors of 4 and 10. This created new models with flow path gradients of 0.4 and 0.1 times the original values.

### 2.3.4. Flow Path Length

[38] The flow path length defines the distance from points in a catchment to the stream into which the points drain. It is dependent on the density of the stream network, as well as the shape of the catchment. The distribution of flow path lengths determines the distances over which hillslope routing takes place, and consequently can be expected to have an influence on the residence times of water. The flow path length can be adjusted for the STREAM model by making differing assumptions about the threshold flow accumulation at which a point in the catchment is defined as a stream. For the baseline Maimai model, a flow accumulation of 12 cells was found to give a comparable definition of the stream network to that observed in practice. To test the role of flow path length in determining residence times, flow path lengths were calculated on the basis of threshold accumulations of 5, 100 and 390 cells.

### 2.3.5. Deep Groundwater Processes

[39] One hypothesis regarding residence time distributions is that catchment MRTs can be significantly increased by contributions of a small volume of deep groundwater with a very long residence time. The role of this potential mechanism was studied by invoking the deeper groundwater store within the Maimai catchment model. The store was assumed to be recharged by a constant flow from the shallower groundwater store. A feasible recharge rate was estimated from the Maimai streamflow record, by taking the lowest recorded flow and assuming a constant recharge equivalent to this rate. The lowest recorded flow was assumed to represent the level of base flow that is sustained even when the catchment is under drought conditions, and hence to be representative of a very slowly responding deep source of water. Discharge to the stream network was assumed to follow the same flow path as the shallower flows, but with a much lower hydraulic conductivity, leading to much longer residence times.

### 2.3.6. Riparian Storage

[40] Riparian zones have been observed to act as buffers to pollutant transport [*Muscutt et al.*, 1993; *Lowrance et al.*, 1997] which suggests that they often play an important role in catchment functioning. It is clear that in some catchments the presence of flat-bottomed, alluvial, riparian zones can store a significant volume of water, where a high degree of mixing can occur. Although not believed to be significant in the Maimai catchment in terms of total storage [*McDonnell*, 1990; *McGlynn and McDonnell*, 2003], the potential influence of a riparian storage was investigated for its effect on residence times. All subsurface and groundwater flows from the catchment were assumed to discharge into a 10 m wide riparian store where simple mixing takes place prior to discharging into the stream.

## 3. Results

### 3.1. Baseline Model

[41] The model representation of the soils in the Maimai catchment assumed homogeneity in terms of the *CV* and *CL* parameters and assumed that the *FC* and *SC* parameters varied simply as a function of the soil depth. These latter two values together with $\varphi$ were based on previous measurements of soil physical properties in the catchment [*Pearce et al.*, 1986]. The near surface and shallow groundwater rate parameters, *KS* and *KG*, were also assumed to be homogenous across the catchment. For the baseline model there were therefore four parameters to be calibrated for the flow simulations, and a further parameter (*EPUz*) to be calibrated for simulation of the tracer response. *EPGw* was assumed equal to 1. A range of criteria was used for the model evaluation as follows: (1) Nash-Sutcliffe [*Nash and Sutcliffe*, 1970] efficiency of flow predictions, (2) Nash-Sutcliffe efficiency based on log (flow) values, (3) ratio of shallow groundwater hillslope runoff to near surface bypass flow, and (4) mean residence time of water.

[42] Over 3000 simulations, varying each of the four flow parameters, were carried out and compared, using the first three criteria above to select an appropriate parameter set for the baseline model. A further set of simulations was then run to calibrate a value for *EPUz* using the MRT criteria. After initial tests of the tracer response, all the calibration simulations were run for a period of 3 years (with a basic model time step of four hours), to ensure that full tracer recovery was achieved, and that consequently the calculated MRT values were accurate for the model.

[43] In common with model applications by other authors [e.g., *Beven and Binley*, 1992; *Freer et al.*, 1996] it was found that acceptable simulations of flow (defined here as

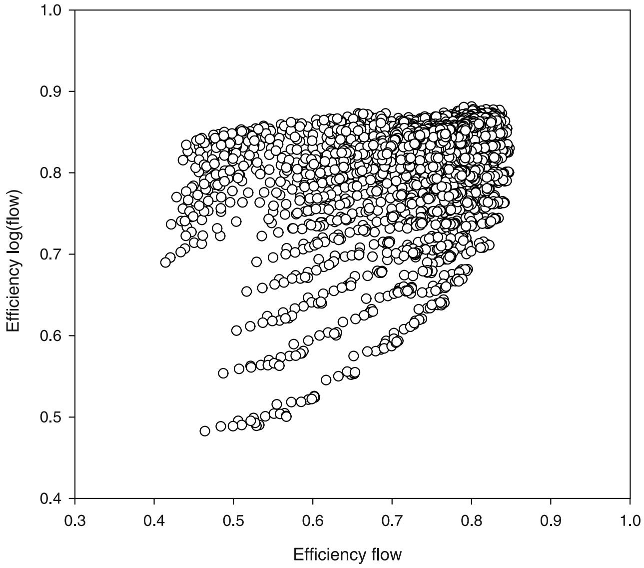


**Figure 2.** Nash-Sutcliffe efficiency of flows and efficiency of log (flows) for 3120 simulations used to calibrate baseline flow model.

Nash/Sutcliffe efficiency of flow > 0.8 and of log (flow) > 0.8) could be found using a broad range of parameterizations of the model. These two criteria alone reduced the number of acceptable simulations from 3120 to 622 (20%) (Figure 2). The discrimination between these simulations on the basis of the relative flow proportions (with an acceptable proportion of hillslope runoff defined as lying between 0.6 and 0.8) further reduced the number of acceptable simulations to 42 (1.3% of the total) (Figure 3). The addition of this criterion was therefore important in discriminating between the different parameter sets. The 42 parameter sets that were deemed as acceptable all had values of *CV* and *CL* of 0.0025 $s^{-1}$ and 0.05 $s^{-1}$, respectively, but with varying values for *KG* and *KS*. One pair of values for *KG* and *KS* was selected for the baseline model from these 42 parameter sets.

[44] In terms of the tracer response, a similar result to *Vaché and McDonnell* [2006] was found; namely that an effective porosity value of *EPUz* = 0.4 was necessary to achieve mean residence times comparable to the four months previously estimated [*Pearce et al.*, 1986]. The calibration of this value will be discussed in greater detail in the analysis of the unsaturated zone processes. The resulting baseline model predictions of streamflow are plotted with the measured stream discharge in Figure 4. In Figure 5 the modeled response in the stream to a pulse input of tracer is illustrated as a time series plot, and also as a cumulative plot showing the recovered percent of applied tracer through time.

### 3.2. Hillslope Flow Processes

[45] Hillslope flow processes were examined by excluding the unsaturated zone and near surface runoff from the STREAM model. All of the effective precipitation was then routed directly into the shallow groundwater hillslope runoff component of the model. Applying the same value of *KG* as for the baseline model, the MRT of this model simulation was reduced to only 5 days. Thus the hillslope flow processes have only a small control over the residence time within the baseline model. The hillslope flow model was also recalibrated for *KG* using three of the criteria for model evaluation (defined above) as objective functions (runoff ratio was not relevant as only one flow path was invoked in this case). The results of this calibration demonstrated that only a poor simulation of the streamflow could be achieved, with a highest Nash-Sutcliffe efficiency of 0.4. The MRT of this simulation was even further reduced to a typical value of 2 days, demonstrating its incompatibility with the observed tracer behavior within the catchment. This result is also in line with the findings of *Vaché and McDonnell* [2006].

[46] The sensitivity of the catchment MRT to the inclusion of an effective porosity within the hillslope flow component was tested by running a set of simulations using the baseline model and with *EPGw* varying between 1.0 and 0.1. These results are shown in Figure 6. With *EPGw* = 0.1 the catchment MRT increased to a maximum value of 155 days, representing a residence time of 30 days in the hillslope itself. However, with a value of *EPGw* = 0.2 the hillslope residence time was only 15 days.

### 3.3. Unsaturated Zone Processes

[47] The results of the hillslope flow model experiments demonstrated the importance of the unsaturated zone representation within this model in controlling the catchment MRT. With the residence times for the near surface runoff even shorter than the hillslope runoff, 95% of the total tracer residence time in the baseline model was calculated to be within the unsaturated zone.

[48] The sensitivity of the catchment MRT to *EPUz* was also examined by varying its value from 0.1 to 1.0, while maintaining other parameters of the baseline model. The results of these simulations in terms of the MRT are

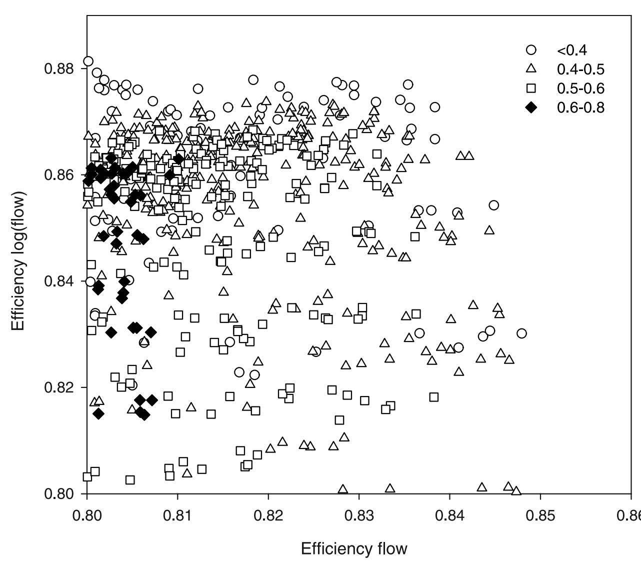


**Figure 3.** Relationship between three objective criteria used for calibration of the flow model. Simulations with Nash-Sutcliffe efficiency of flows and efficiency of log (flows) $\geq$ 0.8 are plotted for a range of values of the ratio of shallow groundwater flow to near surface flow. Simulations satisfying the criteria for hillslope runoff proportion are shown as solid diamonds.

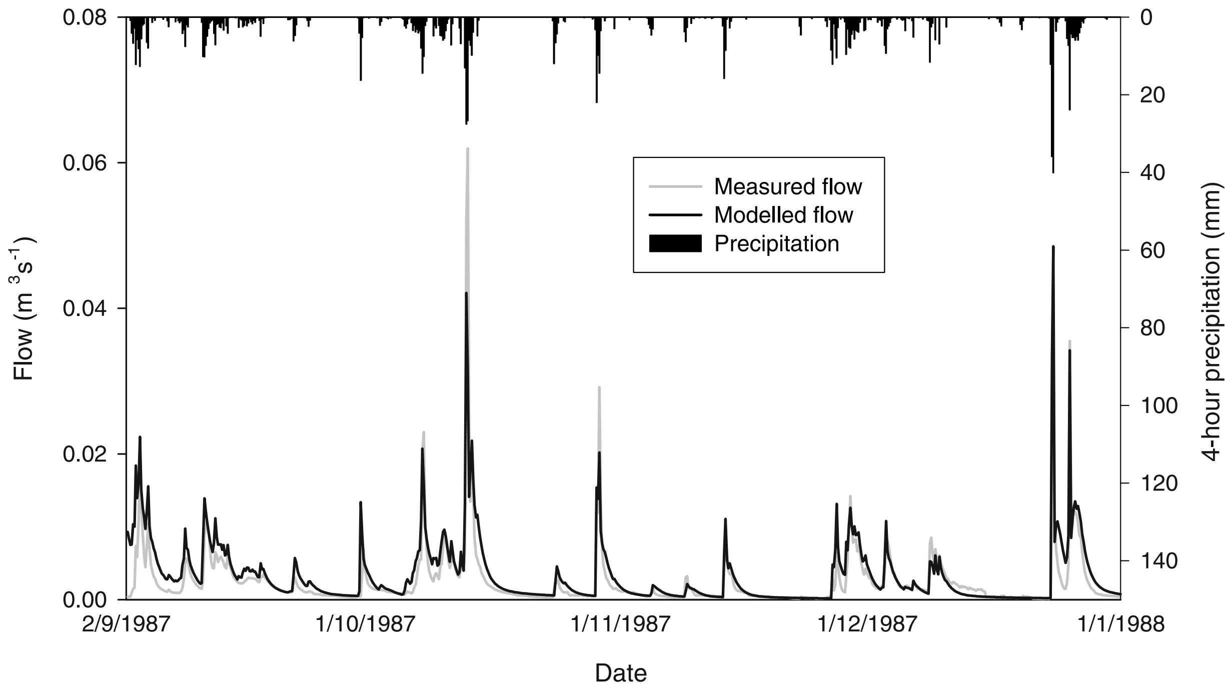


**Figure 4.** Rainfall, measured flow, and modeled flow for the Maimai catchment September–December 1987.

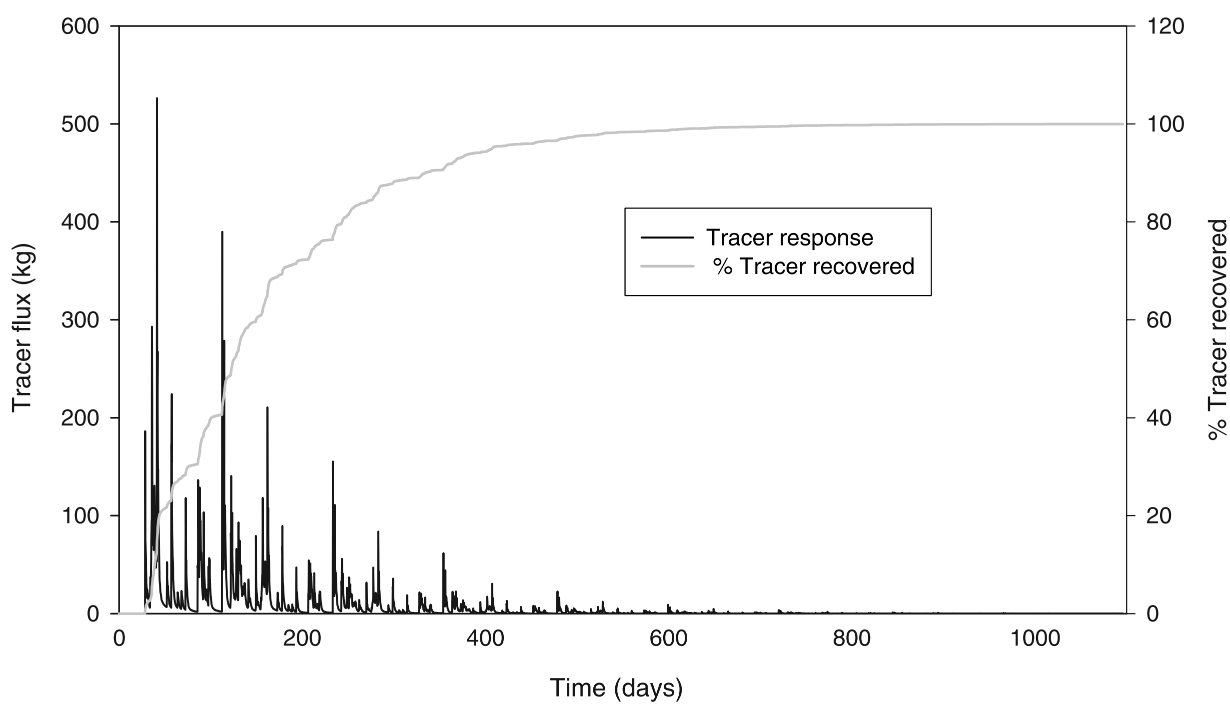


**Figure 5.** Modeled tracer response over 3 years to a pulse input of tracer for the baseline Maimai model. Meteorological data were cycled over a 4 month period. The cumulative fraction of recovered tracer is also shown.

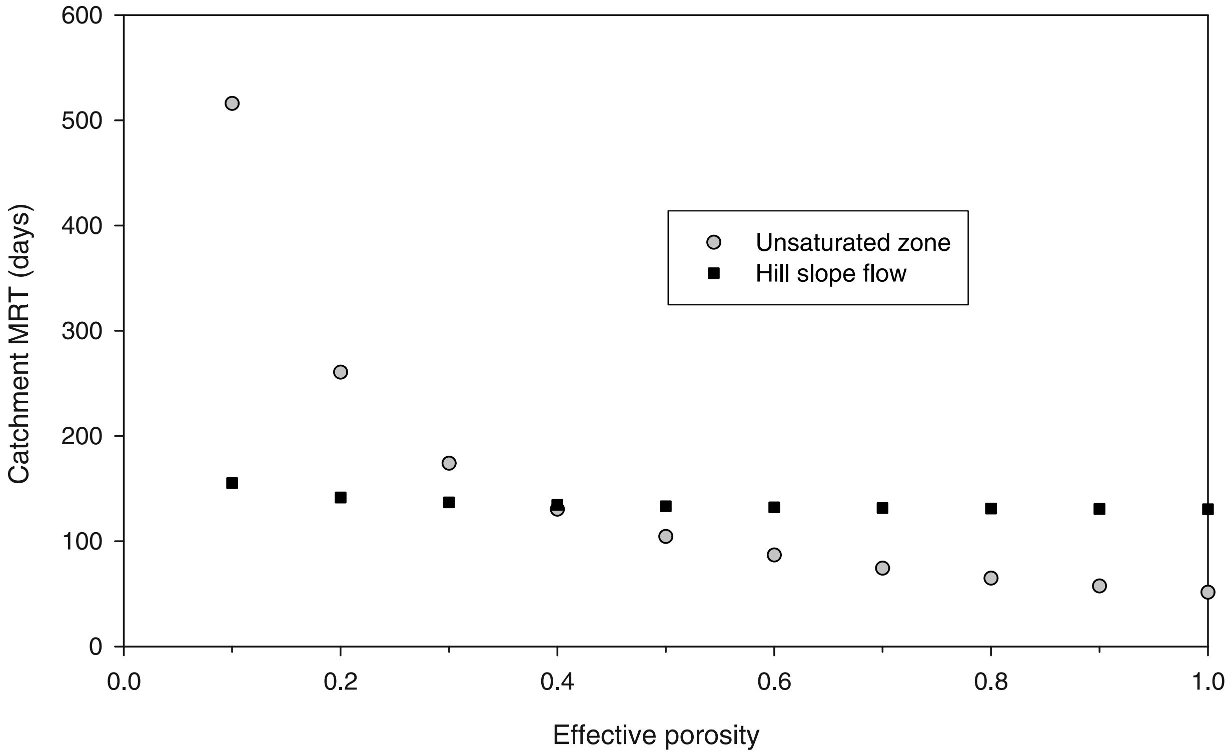


**Figure 6.** Sensitivity of modeled catchment MRT to value of effective porosity for the hillslope flow component and the unsaturated zone.

illustrated in Figure 6. With an effective porosity of 1 the MRT of the simulations was reduced to 51 days. This representation would infer that there was no immobile water in the unsaturated zone and that the tracer was transported by pure advection with the water flows. The MRT of the simulations increased in proportion to (1/*EPUz*), giving an MRT of 516 days with a value of *EPUz* = 0.1.

### 3.4. Flow Path Gradient

[49] The mean flow path gradient for the baseline model of the Maimai was 0.56. The two experimental models tested by manipulation of the Maimai DEM had mean gradients of 0.14 and 0.056, respectively. The MRT values of simulations performed with these two models, with all other parameters kept identical to the baseline model, were increased from 130 days to 133 and 136 days, respectively. Given the results from the model based purely on hillslope flow routing, with no unsaturated zone, this was equivalent to a 60% and 120% increase in the residence times within the hillslope routing component of the model.

### 3.5. Flow Path Length

[50] The catchment mean flow path length was modified from 34 m to 20 m, 63 m and 149 m for the model experiments on the basis of different definitions of the stream network. The last of these models was based on only one stream cell within the whole of the Maimai catchment. The MRT values of the simulations were 129 days for the 20m average flow path length, 146 days for the 63 m average length and 206 days for the 149 m average length. These data are plotted in Figure 7, which shows that the MRT is approximately linearly related to the average flow length.

### 3.6. Deep Groundwater Processes

[51] A feasible deep groundwater recharge rate was estimated from the streamflow hydrograph at 80 mm per year. Two further parameters control the influence of the deep groundwater behavior within the model: the initial depth of the deep groundwater store, *DGI*, and the groundwater conductivity, *KDG*. An indicative value for the groundwater conductivity was estimated at $10^{-8}$ m s$^{-1}$ on the basis of literature data for similar geological strata. This value is used purely to give an indication of the potential sensitivity of the catchment MRT to a small fraction of slowly transported water. The selected *KDG* permitted a value to be calculated for *DGI* (= 430 mm) to achieve steady state conditions within the deep groundwater component of the model. A simulation using these parameter values was run for a total length of 40 years, to ensure full tracer recovery from the deep groundwater component. The results of this simulation gave a catchment MRT of 167 days, an increase of 37 days over the baseline model. The total flow contribution from the deep groundwater accounted for only 1.6% of the total stream runoff, but the mean residence time of the deep groundwater itself was 7.4 years. The values of the objective functions for this simulation were largely unaffected by the inclusion of the deep groundwater with the Nash-Sutcliffe efficiency remaining the same as the baseline model at 0.81, while the log efficiency value increased very slightly from 0.86 to 0.87.

[52] Additional simulations were carried out to test the potential significance of deep groundwater flows in situations with a higher recharge rate or lower groundwater

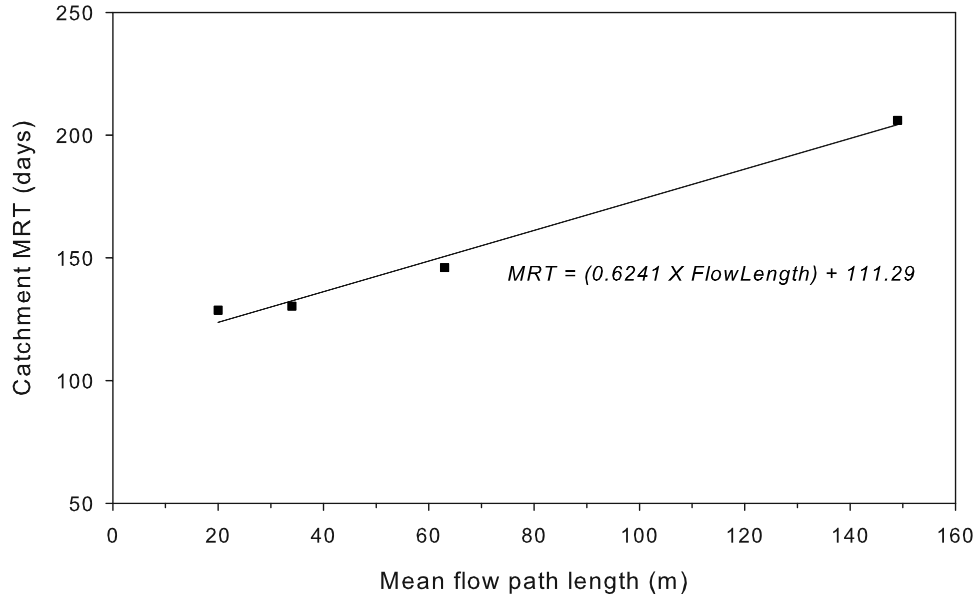


**Figure 7.** Relationship between mean flow path length and modeled catchment MRT.

conductivity. A doubling of the recharge rate, to 3.2% of the total stream runoff, was calculated to increase the catchment MRT to 202 days. Alternatively, decreasing the groundwater conductivity by a factor of 10 (with a corresponding increase in the initial condition for the depth of the groundwater store), resulted in an increase in the catchment MRT to > 293 days. After simulation of a 100 year period, only 77% of the tracer leached to the deep groundwater component had been recovered.

### 3.7. Riparian Storage

[53] A 10 m wide riparian storage was defined along all stream cells of the baseline Maimai model. For simplicity, the value of the riparian rate parameter (*KR*) was set to the same value as that of the shallow groundwater rate parameter (*KG*). The total depth available for mixing in the riparian zone was defined by the soil depth. A simulation based on these definitions caused the calculated MRT of the baseline model to increase from 130 days to 142 days. The Nash-Sutcliffe efficiency of the flow predictions was unaffected by the inclusion of the riparian store.

## 4. Discussion

### 4.1. On the Virtual Experiment Approach

[54] While modeling studies have begun to use stream MRT as additional criteria for model evaluation [*Uhlenbrook and Leibundgut*, 2002] and as a means to reject model structures [*Vaché and McDonnell*, 2006], there are still too few observational studies conducted to date to inform what are the fundamental controls on stream water mean residence time. While additional field studies are needed, expense and time preclude a large number of these on the immediate horizon. In this paper we have used the *Weiler and McDonnell* [2004, 2006] virtual experiment approach to seek new understanding of the relative importance of hillslope and catchment runoff processes on derived stream MRT. Our underlying rationale was that, as a catchment-averaged indicator, the MRT can be considered additive—constructed from the accumulation of residence times in sequential stages of hydrological transport, as well as sequential transport through geographic space. By using our conceptual understanding of the hydrological processes operational in the well-studied Maimai M8 catchment, we performed a set of model experiments using a semidistributed conceptual hydrological model to simulate the transport of a conservative solute tracer. The experiments explored how different properties of a catchment system could influence the overall behavior of the catchment in terms of its MRT.

[55] Table 2 summarizes the results of the model experiments quoting the range of mean residence times calculated for each component of the model. The catchment MRT represents the combined effect of these component MRT

**Table 2.** Summary of Model Experiment Results in Terms of Modeled MRT for Each Model Flow Component[a]

| Property/Parameter | Model Component | Values Tested | Modeled Component MRT, days |
|---|---|---|---|
| GW effective porosity | groundwater hillslope routing | 1.0–0.1 | 5–30 |
| UZ effective porosity | soil water balance | 1.0–0.1 | 46–511 |
| Flow path gradient | groundwater hillslope routing | 0.056–0.56 | 5–11 |
| Flow path length | groundwater hillslope routing | 20–149 m | 4–81 |
| Groundwater hydraulic conductivity | deep groundwater | $10^{-7}$–$10^{-8}$ cm s$^{-1}$ | 2700–>13300 |
| Riparian width | riparian storage | 0, 10 m | 0, 12 |

[a]The catchment MRT represents the combined effect of these component MRT values.

values. The results demonstrate how the different processes represented in the model of the Maimai catchment interact in a complex manner to generate the average behavior that is summarized by the catchment MRT. We used the findings of the model experiments to consider more broadly how residence times of water in different catchments may be controlled by several different key properties of the system.

[56] Our baseline model of the Maimai catchment was constructed to reflect current conceptual understanding of the most important hydrological processes in that catchment. This model indicated that transport in the unsaturated zone played a very important role in determining the mean residence times of water. The model representation of the unsaturated zone was quite simplistic, but provided a mechanism for explaining the mixing and lags necessary to explain the behavior in the catchment. The effective porosity parameter in the unsaturated zone proved to be necessary to achieve residence times of the correct order of magnitude for the catchment. This parameter was purely conceptual in the manner in which it is implemented within the STREAM model, but nevertheless provided a surrogate for commonly observed physical processes relating to mobile and immobile transport in soils. Under stormflow conditions the model representation generated near surface runoff. This flow component is routed rapidly to the stream network and the residence time is therefore not dependent on topographic location. However, the water is still assumed to have mixed within the soil profile, and thus retains the MRT of the unsaturated zone processes. In practice, the occurrence of processes such as infiltration excess runoff may lead to a fraction of new water reaching the stream network directly under stormflow conditions.

### 4.2. Role of Deep Groundwater

[57] From the few observational studies that have been completed in steep headwater catchments, bedrock permeability has been shown to be a first-order control on the direction of water aging in the subsurface—from downslope aging in catchment systems with largely impermeable underlying bedrock [*Stewart and McDonnell*, 1991] to vertical aging in the soil profile (and into the bedrock) in catchments with highly permeable bedrock. While our virtual experiments within the Maimai catchment retained the overall character of largely impermeable bedrock characteristic of the site, our virtual experiments show the potential influence on residence times of a small proportion of deep groundwater mixing with the hillslope runoff. Our simulations suggest that only a small proportion of the flow needs to be routed via a long residence time deep groundwater flow path to make a significant difference to the stream water MRT. The potential influence of deep groundwater also highlights the fact that a measure of the catchment MRT alone does not adequately characterize the behavior of a catchment because of the variability in the nature of the residence time distribution. Thus it may be necessary to acquire a range of data, for example to assess the age of groundwater through the use of alternative hydrochemical and isotopic tracers.

[58] *Asano et al.* [2002] observed a similar phenomenon in their experimental catchment where mean residence times of streamflow were found to be significantly longer than those of adjacent soil water as a result of contributions from lateral groundwater flow through the bedrock.

### 4.3. Flow Path Length Versus Hillslope Gradient

[59] Our virtual experiments on the topographic influences on MRT suggested that the flow path length is a more important control on residence times than the hillslope gradient. Both the flow path length and hillslope gradient within the Maimai catchment are quite extreme compared to most areas, with a very short hillslope lengths and steep gradients throughout the catchment. These factors undoubtedly contribute to the importance of the unsaturated zone in determining the MRT for the Maimai catchment. The analysis of flow path length in particular showed that the MRT could increase quite significantly for a catchment where the hillslopes are longer. This topographic attribute tends to vary with scale, usually with longer mean flow path lengths in mesoscale (10–1000 $km^2$) catchments compared with miniscale (1–10 $km^2$) catchments. This is because channel initiation is related to topographic slope as well as upstream contributing area [*Giannoni et al.*, 2005]. *McGuire et al.* [2005] found a significant relationship between both median flow path length and median flow path gradient and MRT. It is notable that the catchments that they studied had significantly longer flow path lengths (median 125–290 m) compared with the Maimai catchment (average 34 m). This would account in part for their longer MRT values, although the slope of the relationship calculated from the STREAM model experiments is shallower than that found by *McGuire et al.* [2005]. This latter observation indicates that in the Maimai model, flow path length had a weaker influence on the MRT than that observed by *McGuire et al.* [2005] for the HJA Andrews catchments, possibly as a result of higher modeled groundwater transport rates.

### 4.4. Riparian and In-Stream Storage

[60] The simplified representation of riparian storage examined in this study did not exert a particularly strong control on the MRT of catchment waters. A relatively large riparian store was defined in the simulations (10 m wide and with the full depth of soil available) in relation to the measured riparian dimensions of the first-order streams reported in this catchment by *Mosley* [1979]. This suggests that the size of the riparian storage that is potentially available would not be adequate to account for the mixing and lag that is observed in the stream water. *McGlynn and McDonnell* [2003] examined the relative contributions of riparian and hillslope zones to runoff in the Maimai catchment for a series of storm events. They showed that water sourced from riparian zones dominated the runoff between events and during the early part of storm events. However, the riparian zones exhibited poor buffering of hillslope runoff during larger events. This indicated that the volumetric storage within the riparian zones was small relative to the hillslope storage, which is consistent with the relatively small influence on MRT calculated by the virtual experiments. In a much larger catchment it is possible that there would be greater influence of the riparian zone, where, for example, there is a wide flat valley with deep alluvial soils that can store much greater volumes of water. In such a situation hyporheic exchange could also result in lengthened residence times with the potential for reverse flows from the

bed of the stream to the unsaturated zone, under certain conditions.

[61] The model experiments carried out in this paper did not involve any in-stream routing of flows or tracer. For the Maimai catchment, the assumption that in-stream residence is insignificant relative to other processes is probably quite reasonable, given the short length of stream reaches and the impermeable nature of the underlying bedrock. A recent study by *Gooseff et al.* [2005] investigated the role of transient storage both within streams and in stream hyporheic zones for a 300–400 m reach of first and second-order streams. The results from these experiments gave typical mean residence times of only a few hours for a bedrock stream with no hyporheic zone. However, a reach of stream overlying an alluvial aquifer was found to have a much longer mean residence time of the order of 50 days. Clearly for larger catchments with long reaches of stream where there are strong hyporheic interactions, these substream influences on catchment MRT values could be very important.

### 4.5. Going Beyond These Virtual Experiments

[62] We recognize that the general applicability of these findings (beyond the Maimai test case) will only become apparent once further field-based MRT studies have been undertaken on different catchments and under different climatic conditions (e.g., drought, high-flow periods). Nevertheless, the key findings from this set of virtual experiments provide some indications of catchment characteristic controls on MRT.

[63] The baseline model for the Maimai catchment defined a single soil type, assumed to be homogenous across the catchment. Although the unsaturated zone processes were found to be significant, the results did not show how MRT might be affected by the presence of different soils. A recent study by *Soulsby et al.* [2006] found a strong relationship between catchment MRT and soil type. They used a classification of soil type based on hydrological functioning; the Hydrology of Soil Types (HOST) [*Boorman et al.*, 1995] to relate residence times to the distribution of soils within a catchment. The success of this approach in explaining much of the observed variability appears to support the findings of the model experiments carried out here, as the behavior of the unsaturated zone processes in terms of storage and effective porosity will be closely linked to the soil physical properties. Consequently, the soil classification provides an effective spatial carrier of these data.

[64] Our results have a number of implications in terms of developing indices for catchment characterization. First, it is clear that MRT, although it provides an appealing summary of the temporal behavior of a catchment, is a complex index that does not uniquely define the manner in which water is stored within a catchment system. The model experiments demonstrated that there are several different mechanisms that can account for residence times within a catchment, such that two different catchments with similar MRT values may function quite differently. This has been illustrated by disaggregating the catchment MRT into a series of component residence times relating to different processes within the catchment. Traditional experimental approaches for calculating catchment MRT, by necessity, make some assumptions about the nature of the residence time distribution. Most commonly the exponential distribution is applied [e.g., *DeWalle et al.*, 1997; *Burns et al.*, 1998], although more recently *Kirchner et al.* [2000] argued that the gamma distribution is more appropriate. Our analysis of individual components of the catchment MRT demonstrates that the form of the residence time distribution is likely to vary considerably between catchments, depending on the dominant internal runoff processes.

[65] Some simple relationships between catchment characteristics and component residence times have been identified through the virtual experiments; for example in relation to the flow path length and the influence of deep groundwater. If similar relationships could be developed for each of the main catchment processes, then together they could provide a powerful means of defining the expected response of a catchment. Such a capability would be of value to assist with scaling studies and the transfer of hydrological understanding to ungauged basins, a principal target of the International Association for Hydrological Sciences Decade of Prediction in Ungauged Basins [*Sivapalan et al.*, 2003].

[66] Evaluation of the MRT is likely to be of particular value in the context of understanding future catchment responses to environmental or land management changes [*Zoellmann et al.*, 2001; *Murray and Buttle*, 2005]. The MRT defines a very different feature of catchment behavior to other spatially integrated observational data such as streamflows and chemical concentrations that are commonly used for evaluating hydrological and water quality models [*Hooper et al.*, 1988]. Whereas performance capabilities of hydrological and water quality models have been found to be adequate for reproducing current day water quality [*Krysanova et al.*, 2005], important questions remain over their reliability to predict into the future [*Bloschl and Zehe*, 2005]. This is because of high uncertainties regarding understanding of how catchment waters are stored and mixed within the soil-groundwater system. The utilization of MRT within a modeling context appears to offer considerable scope for improvement in this regard.

[67] An important issue regarding the value of model experiments is that the results of the experiments can only reflect the capabilities of the model in explaining the flow and transport processes occurring in a catchment. Many of the processes represented within the STREAM model are a gross simplification of reality. For example, the unsaturated zone is represented by a simple box in which all water is fully mixed, when we know that in practice infiltration into the unsaturated zone occurs over time and that in reality there is likely to be a distribution of residence time that varies with depth. However, models of this type have been commonly used to represent hydrological processes at a catchment scale, and found to be more appropriate in terms of their parameterization needs than more complex physically based models that have large numbers of spatially varying parameters [*Beven*, 1989]. Although the STREAM model has not yet been widely applied, previous models on which it was based have been found to be applicable to a wide range of catchments within Scotland, and to provide an appropriate hydrological foundation for modeling diffuse pollution at catchment scales [*Dunn et al.*, 1998, 2004, 2006]. The use of a multiobjective criteria approach to model calibration helps to ensure that the modeled processes are

consistent with several known features of the runoff [*Guntner et al.*, 1999] including, in this case, the proportions of flow generated by different pathways. Indeed, integration of tracers within a hydrological modeling methodology potentially provides a mechanism for improving the parameterization of such models. A recent application of the STREAM model to a small (0.7 $km^2$) catchment in north east Scotland (S. M. Dunn, and J. R. Bacon, Using tracer data in conceptual modelling of transport processes and water residence times, submitted to *Journal of Hydrolology*, 2007) found that information gleaned from tracer data was highly beneficial in supporting the model structure and parameterization, and highlighting features of the runoff processes that could not be interpreted from streamflow data alone.

[68] Given the limitations of the model and simplifications of reality that it makes, it is important that virtual experiments of this type are viewed as part of an iterative scientific methodology that integrates the modeling together with field experimentation and further model adaptation and development. The modeling does offer insights into possible mechanisms that can be very difficult to measure in field experimentation and where field experimentation is also subject to many experimental uncertainties. This latter aspect also needs to be considered within the model application, as both input data (e.g., rainfall, evapotranspiration, soil properties etc.) and model validation data (e.g., streamflow observations, tracer measurements etc.) can be subject to quite high uncertainties [*Harmel et al.*, 2006]. Further development of appropriate modeling methodologies is necessary to account for these uncertainties within the model applications. Outcomes from the modeling experiments have the potential to guide the selection of suitable methodologies for future field experimentation. For example, *Zoellmann et al.* [2001] presented an interesting field methodology for attempting to disaggregate the residence time in the unsaturated zone from that of the saturated zone through the use of combined solute and gaseous tracers. Such an approach could provide an interesting methodology for supporting the hypothesis generated in this study in relation to the importance of the unsaturated zone. In this way there is the potential to build a synergistic approach to science that unites field and laboratory specialists with computer modelers in a manner such as that advocated by *Seibert and McDonnell* [2002].

## 5. Conclusions

[69] This study has investigated the relationship between residence times of water and a range of catchment properties and processes, as represented by a semidistributed conceptual model. The model experiments have generated a new set of hypotheses about the most significant controls on residence times. One of these hypotheses is that in a small steep catchment, with an impermeable geology, the primary control on the mean residence time is storage within the unsaturated zone. Another is that in catchments where a small component of the streamflow is generated by deep groundwater, the mean residence time for the catchment is significantly extended by the groundwater contribution. The experiments also support findings from other studies in terms of a relationship between flow path length and residence time. Perhaps most importantly, the study has highlighted how the catchment MRT can be considered to be constructed from a series of component residence times, each of which individually should be much easier to relate to simple characteristic properties of the catchment. This provides a potential mechanism for extrapolating results from experimental catchments to other areas where fewer hydrometric and chemical data are available. The results from the study are of value both in the further development of transferable catchment indices and for improving conceptual catchment-scale models to ensure that they are appropriate for applications requiring prediction of future catchment responses to environmental or land management changes.

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