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Modeling Base Flow Soil Water Residence Times From Deuterium Concentrations

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Three approaches to determining mean soil water residence times in a steep headwater catchment were investigated. The deuterium concentrations of soil water collected from 11 suction cup samplers at the Maimai M8 catchment were determined weekly for 14 weeks and the results compared with those of rainfall in the same period. Deuterium variations in the suction samples were considerably delayed and diminished compared with the rainfall, indicating significant storage times and mixing with soil water. Soil matrix water at shallow levels (~200 mm depth) in unsaturated soils was relatively responsive to fresh input, but deeper water and water near the stream subject to occasional water table rises showed much less variation. Steady state and non–steady state exponential models gave similar mean residence times, ranging from 12 to more than 100 days for different locations. Three groups of soil water response were defined, comprising shallow, medium and deep (near-stream) soil locations based on the mean residence times. The nonsteady models revealed considerable week-to-week and longer variations in mean residence time for shallow soil (SL4), but indicated that steady state models could adequately represent the system in the overall period investigated. In the third approach, model types and parameters that gave the best fits to the soil water deuterium concentrations were determined. Exponential and especially dispersion models were the most satisfactory. Weighting the input (rainfall δD) partially or fully with the amount of rainfall gave much worse fits than with the unweighted input, showing that much of the rainfall bypasses the soil matrix. The best fitting dispersion model (designated DM2) yielded the most accurate mean residence times: 13 days for shallow soil (SL4), 42 days for soil at 400 mm depth (SL5), both at midslope locations, and 63 days for soil at 800 mm depth near the stream (SL2). Capillary flow was important for the unsaturated shallow soil (SL4), while advection and hydrodynamic dispersion (mixing) were more dominant for the periodically saturated (SL5) and the generally saturated (SL2) soils.

INTRODUCTION

Stable isotopes have been used increasingly in recent years to investigate the role of "new" or storm water, and "old" or prestorm water, in producing storm runoff in catchments [e.g., *Sklash et al.*, 1976; *Rodhe*, 1981]. The results have indicated that "old" water, generally interpreted as groundwater, plays a surprisingly active and possibly even a dominant role in producing stormflow. This is in conflict with hydrometric studies, particularly as applied to hillslopes, which have emphasized the importance of processes allowing rapid flow of rainwater to channels [*Mosley*, 1982].

Studies in Maimai catchment, west coast, New Zealand have illustrated this conflict in sharper relief. The catchments are steep and have shallow soils, and streamflow is very responsive to rainfall [*Pearce et al.*, 1976]. Hydrometric studies [*Mosley*, 1979] have shown that water flow in all positions in the catchment (hillslopes and channel system) increases rapidly and simultaneously after rain. It was concluded that rapid flow of new water to the stream in macropores (pores greater than 1 mm) was necessary to explain the rapid response of streamflow. On the other hand, tracer studies using deuterium showed that new water was not greatly involved in streamflow [*Pearce et al.*, 1986; *Sklash et al.*, 1986]. Streamflow following storms contained at most 20–30% new water, and much of that could be attributed to rainfall on channel and bottom slope areas. Deuterium analyses showed that old water was also dominant in flows within the soil mantle of the slopes and valley bottom. The old water contribution increased toward the bottom of slopes [*Sklash et al.*, 1986].

To resolve these differences, more detailed studies of the physical processes within the soil were undertaken. Detailed studies of the soil water status, soil water flows and their deuterium concentrations have been made at the Maimai catchment by *McDonnell* [1989]. The soil water content and flow measurements are described by *McDonnell* [1990]. Interpretation and modeling of the deuterium concentrations in soil water are discussed in this paper.

The objectives are to investigate soil water residence times during stream base flow conditions. Changes in the deuterium concentrations in soil water at different locations in the catchment are related to rain inputs with varying deuterium contents and interpreted in terms of soil water transport processes.

NATURE OF SOIL AND DESCRIPTION OF CATCHMENT

The study was conducted in a steep, humid headwater catchment on the South Island of New Zealand (45°05′S, 171°48′E). The M8 catchment (Figure 1) has been monitored since 1974 [*Pearce et al.*, 1976]. Mean annual rainfall is 2600

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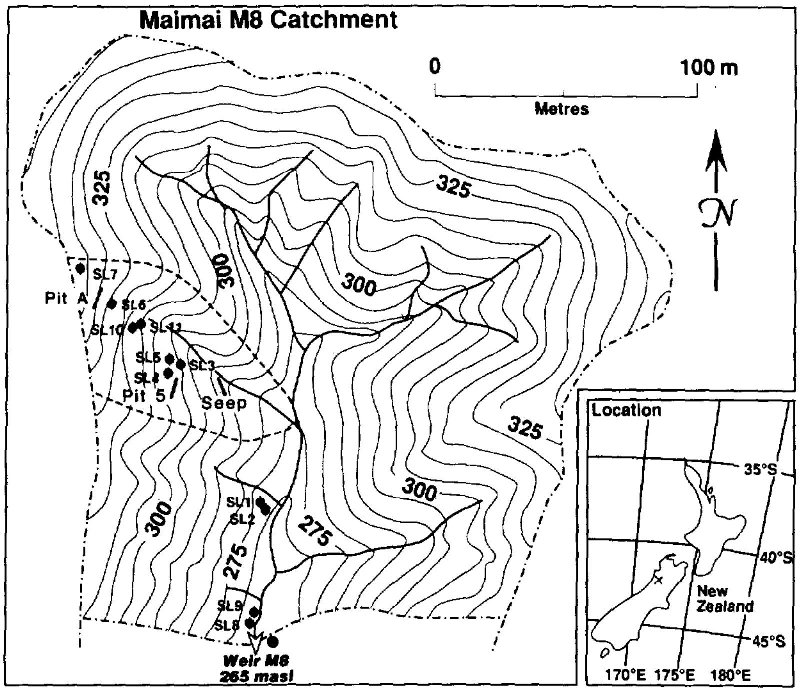

Fig. 1. Maimai 8 catchment showing suction lysimeter (SL) and pit locations.

mm producing 1550 mm of runoff from 1950 mm of net rainfall [*Rowe*, 1979]. Slopes are short (<30 m) and steep (mean 34°), with local relief of the order of 100–150 m. The soil is underlain by a firmly compacted, moderately weathered, early Pleistocene conglomerate, known as the "old man gravels." This unit has been described as "effectively impermeable" [*Mosley*, 1979, p. 795], and "poorly to moderately permeable" [*Pearce et al.*, 1976, p. 150].

Soils in the catchment have developed from the underlying soft, weathered conglomerate and colluvium and are broadly classified as Blackball Hill soils [*New Zealand Soil Bureau*, 1968; *Mew et al.*, 1975]. They show large spatial variability in depth (mean 0.6 m, range 0.2–1.8 m) and character (from podsolized yellow brown earth (YBE), to mottled YBE, to gley soils), and are dominantly stoney throughout their profiles. Mineral soil horizons are overlain by a thick (mean 170 mm) well-developed upper humic horizon. *Webster* [1977] reported average infiltration capacity of the humic layer and average saturated hydraulic conductivity of the upper mineral soil of the order of 6100 mm h^{-1} and 260 mm h^{-1} respectively.

McKie [1978] separated the soils belonging to the Blackball Hill group into seven soil profile classes according to their parent material, slope angle, vegetation and drainage (Table 1). Generally, there is a strong relationship between soil type and slope position as they relate to drainage and soil development processes. The common profile features of the dominant soil profile classes (2, 4 and 5) were derived by McKie from a selection of most commonly occurring properties found in a number of described profiles, whereas the features of the less widespread classes (1, 3, 6 and 7) were based on a representative profile.

METHODS

Rainfall Sampling

Rainfall samples were collected sequentially within the catchment at 2.5 mm, 5 mm and then successive 9.2 mm increments during each storm event [*McDonnell et al.*, 1990]. The collection system was modified from *Kennedy et al.* [1979] and consisted of a 410-mm-diameter funnel, connected at the base to a series of 0.3-L, 0.6-L and then successive 1.0-L bottles. Specially designed glass fittings were constructed and arranged so that each bottle filled before any rain flowed into the following bottle. An air outlet tube maintained a vacuum within each bottle and prevented any mixing between sequential rain samples. A tipping

TABLE 1. M8 Soil Profile Classes Compiled From Data of *McKie* [1978]

Class	Slope Position	Slope	Drainage
1. Shallow podzols	upper nose	15–30	well
2. Podzols	nose and sideslopes	30–40	well
3. Grey podzols	upper hollows	20–40	imperfect
4. Podzolized lowland YBE	sideslopes, upper nose	25–35 (70%); 36–50 (30%)	moderate
5. Mottled YBE	valley basin hollows	26–35 (70%); 10–26 (30%)	imperfect
6. Shallow gley	near-stream (limited)	15–35	poor
7. Gley	near-stream	15–35	very poor

TABLE 2. Suction Lysimeter Depths and Site Characteristics

SL Number	Depth, mm	Distance to Channel, m	Distance to Divide, m
1	400	5	65
2	800	5	65
3	800	30	40
4	200	30	40
5	400	30	40
6	400	25	15
7	300	35	5
8	400	1	75
9	800	1	75
10	400	40	25
11	800	40	25

bucket device was located adjacent to the unit to record rain depth and intensity.

Soil Water and Groundwater Sampling

Both the soil water and the groundwater were sampled using standard Soilmoisture Equipment Corporation 40-mm-diameter, porous cup, suction lysimeters (Table 2). These tubes were inserted at 200, 400 or 800 mm depths in different slope positions within the M8 catchment, as illustrated in Figure 1. A small hand pump was connected to the device and a 60-KPa vacuum was established within the tube. Soil water or groundwater was drawn in through the porous cup and recovered by reattaching the hand pump and pumping the water into a collection bottle. Water was extracted at approximately weekly intervals (September–December 1987), and for one period at daily intervals. This paper discusses the weekly results.

Simple, maximum rise piezometers were constructed using polystyrene floats in 20-mm-OD Perspex tubes. These were located adjacent to each suction lysimeter location to provide the water table height at the time of sampling. This allowed determination of whether the samples were from the unsaturated (vadose) zone or from the saturated (phreatic) zone.

Deuterium Analysis

Deuterium analyses of water samples were carried out by reducing the water to hydrogen over zinc at 450°C [*Coleman et al.*, 1982; *Stanley et al.*, 1984], and analyzing the hydrogen using a VG Micromass 602 mass spectrometer. Results are reported in δ notation relative to V-SMOW where

$$\delta D = \left(\frac{(D/H)_{\text{sample}}}{(D/H)_{\text{V-SMOW}}} - 1 \right) \times 1000‰ \qquad (1)$$

The standard deviation of measurement is ±1.0‰. The results have been normalized assuming $\delta D = -428‰$ for SLAP (standard light Antarctic precipitation) relative to V-SMOW (Vienna standard mean ocean water).

RESULTS

Rainfall

All rainfall samples were analyzed for deuterium. The results were used to calculate amount-weighted average deuterium concentrations of rainfall incident between successive soil water samplings (periods of approximately one week). The weekly rainfall totals ranged from 18 to 152 mm (4 to 20 samples) and comprised one or more rainfall events or parts thereof.

The average δD values of the rainfall events are shown in Figure 2 and the weekly rainfall totals in Table 4. There is considerable variation during the 14-week period of sampling, the δD values showing three approximately sinusoidal cycles of 50‰ peak-to-peak variation. Variations within individual storm events were generally smaller (<30‰). The consistent variation with period of about 5 weeks is regarded as fortuitous, although a seasonal variation of rainfall δD values is expected.

Suction Lysimeter Samples

The suction lysimeter (SL) samples contained water collected from the soil during an hour or so after evacuating the porous cup. The deuterium results for SL4 are given in Figure 2 and the others in Figure 3. The δD values of the suction cup samples show varying responses to the δD variations in the rainfall. Near the stream, SL1 (from 400 mm depth) shows a peak related to, but much smaller than and delayed from, the high δD values of rainfall around September 29 to October 6. SL2 draws from generally saturated soil at 800 mm depth and shows a steady increase in deuterium with very little variation around the trend. This slight increase is considered to be due to the seasonal increase of δD from winter to summer.

Samplers SL3, SL4 and SL5 are from a hillslope hollow location near pit 5 (see Figure 1). SL3 (from 800 mm depth) and SL5 (400 mm depth) show similar small δD variations, although SL3 generally has lower δD. This probably indicates a higher proportion of older, winter-derived water in SL3 drainage. SL4 is the shallowest lysimeter of the three (200 mm), and shows the largest variation (Figure 2). It follows the rainfall pattern closely, but with smaller amplitude and a lag of about 7 days. For the throughflow of pit 5, δD is similar to the results for SL3 and SL5.

The samplers SL6 (400 mm) and SL7 (300 mm) and pit A are situated near the catchment boundary. SL7 shows more variation in δD than SL6, although missing data make the extent of variation in SL6 uncertain. Pit A shows a more rapid and possibly a larger response to rainfall δD variation than SL7.

SL8 (400 mm) and SL9 (800 mm) are close to the M8 weir and, like SL2, show essentially no significant variation in δD apart from a long-term steady increase (see trend line in Figure 3). SL9 is generally in saturated soil. There is a tendency for SL8 to have higher δD than SL9.

In the midslope region, samplers SL10 (400 mm) and SL11 (800 mm) appear to have δD variations quite similar in shape and magnitude to those of SL5 (400 mm) and SL3 (800 mm) at similar locations and depths. All of them are quite smoothed compared to the rainfall.

Samples were also collected from a natural seepage area (the seep) in the subcatchment and from the M8 weir (see Figure 1), although the data are not complete (Figure 3). Results for the seep show very little variation, while the streamflow (M8), which was mainly sampled during base flow conditions, shows some minor variation.

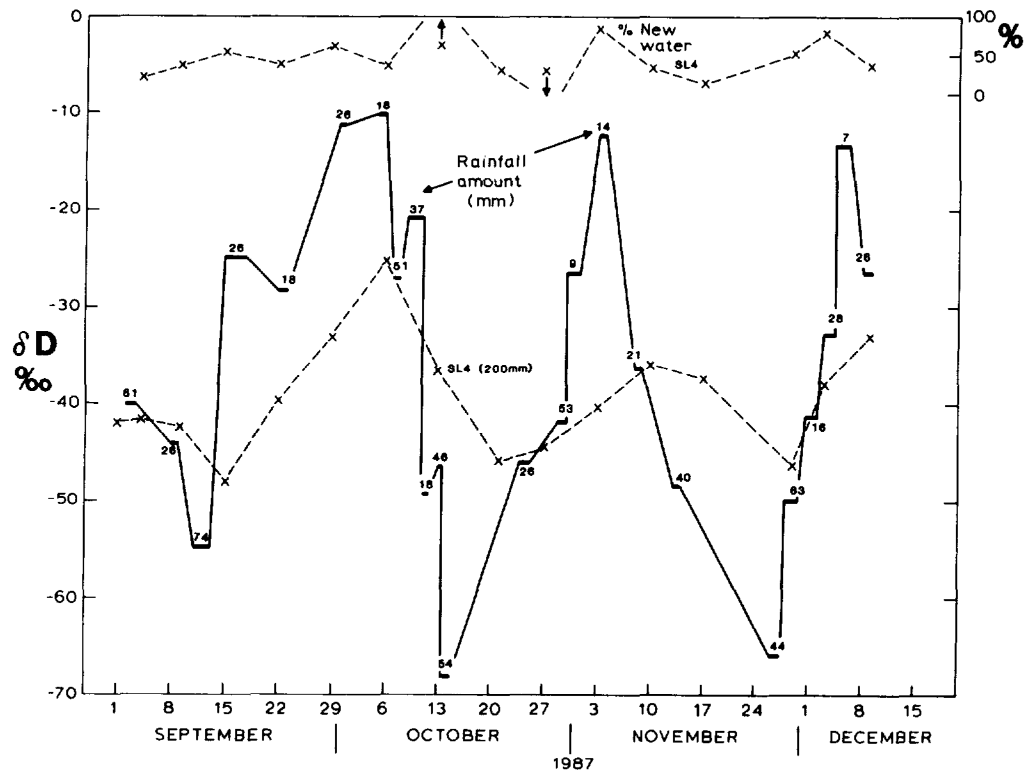

Fig. 2. Deuterium concentrations in rainfall averaged over storm events during September–December 1987. The amount of rainfall is given for each event in millimeters. SL4 deuterium concentrations and new water fractions (from Table 4) are also shown.

Soil Water Residence Times and Flow Models

It is clear from the above results that soil matrix waters at shallow levels and upslope locations show considerable δD responses to rainwater δD input, while deeper waters and near-stream locations display much less variation. This is due to longer water residence times and greater mixing in the latter situations. We use various flow models to describe the mixing, and to deduce the distribution of water residence times in the soil at different locations. We wish to use the residence time distributions to gain knowledge of the nature of the water flow in the soil matrix, but need to know the nature of the flow to choose appropriate models and deduce residence times. Hence, we have adopted an iterative approach to modeling.

First, we have taken the simplest approach and made use of the nearly sinusoidal form of the rainfall δD variation (Figure 2) to evaluate the soil water residence times assuming a steady state well-mixed flow model. In the well-mixed model, incoming rainfall is assumed to mix immediately with all water in the soil "reservoir." This produces an exponential distribution of water residence times. (The model also applies in particular cases where no mixing occurs in the reservoir, but mixing takes place in the outflow). The analysis uses a simple equation given by *Maloszewski et al.* [1983] to determine mean residence times, but takes no account of the short-term variations in the amount of rainfall or consequent variations of flow in the soil.

The second approach allows the model parameter (new water fraction or mean residence time) to vary on week-to-week or longer time scales, while still using the exponential model. The catchment studied has abundant and relatively regular rainfall, but there are big changes in rainfall on short time scales and soil water flows are known to fluctuate widely, along with catchment runoff [*Mosley*, 1979]. This approach reveals the weekly and longer variations in new water fractions or mean residence times.

The third approach investigates different lumped parameter models and particularly their ability to simulate the outputs (deuterium content of soil matrix water and flows). Models that produce the best fits to the outputs are considered to yield the most realistic distributions of water residence times. In addition to model type, the effect of weighting the input δD with the amount of rainfall was investigated. This relaxes the apparently unrealistic steady state model assumption (i.e., that the volumetric flow rate of water into and out of the system is constant).

To carry out the simulations for a given model, the input ($\delta_{\rm in}$) is transformed by means of the convolution integral, to produce the output ($\delta_{\rm out}$), i.e.,

$$\delta_{\rm out}(t) = \int_0^\infty g(t')\delta_{\rm in}(t - t')\, dt' \qquad (2)$$

where $\delta_{\rm in}$ and $\delta_{\rm out}$ are the δD values of rainfall and suction samples or pit flow respectively, and $g(t)$ is the system response function, which specifies the transit time distribution of water within the system [e.g., *Zuber*, 1986]. Different flow models are represented by different system response functions. Here t represents calendar time and the integration is carried out over the transit times (t').

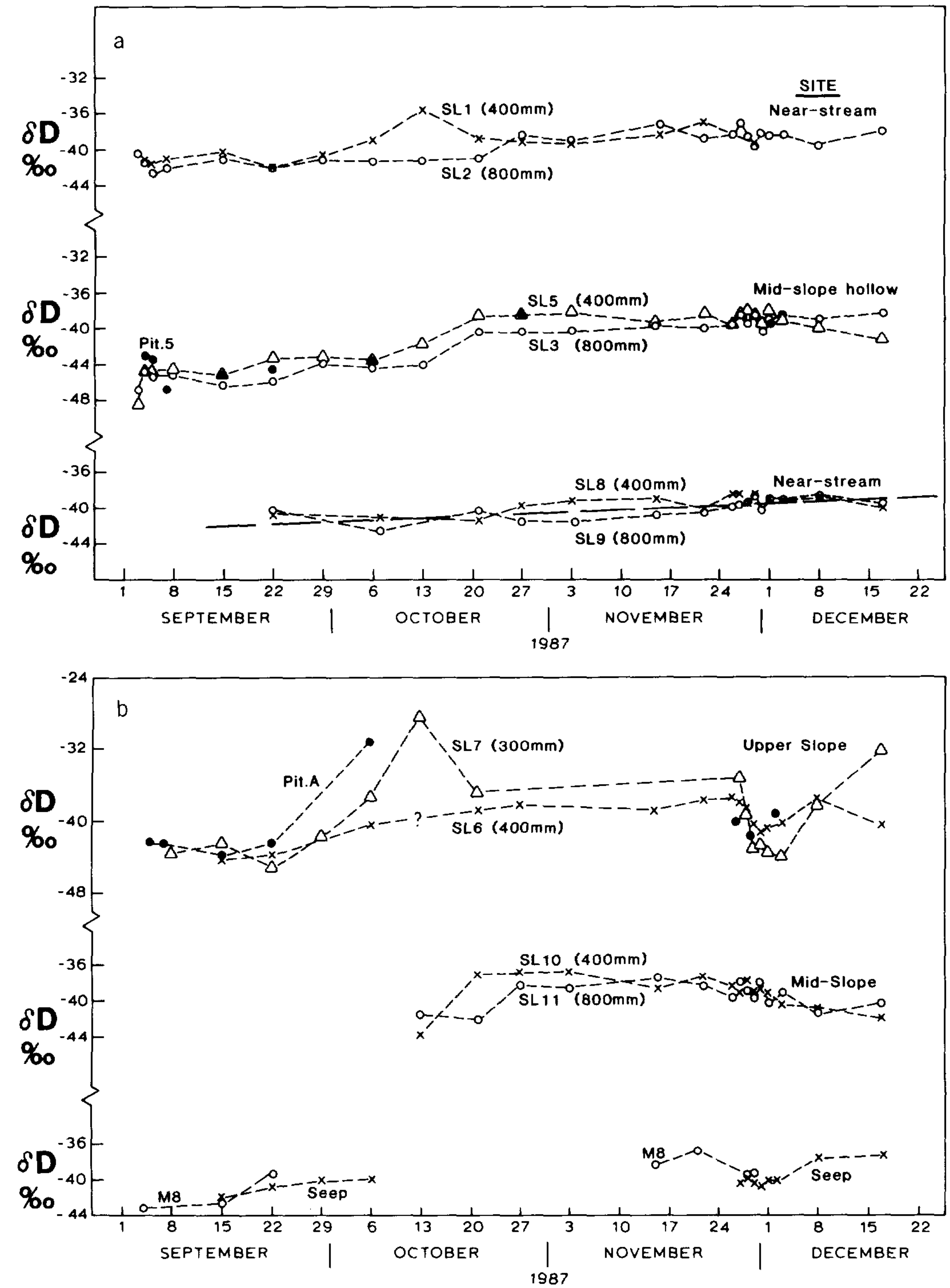

Fig. 3. Deuterium concentrations in suction cup waters, pit flows, natural seepage and M8 streamflow during September–December, 1987, for (*a*) SL1, SL2, SL3, SL5, SL8, SL9, and pit 5 and (*b*) SL6, SL7, SL10, SL11, pit A, M8, and the seep.

The well-mixed or exponential model is characterized by the system response function

$$g(t) = \frac{1}{\tau} e^{-t/\tau} \qquad (3)$$

where τ is the mean residence time of the system.

Two dispersion models were tried. The first (DM1) is the C_{IFF} solution of the dispersion equation [e.g., *Himmelblau and Bischoff*, 1968] given by *Kreft and Zuber* [1978]. In this solution, tracer is assumed to be introduced and sampled in proportion to the volumetric flow of water in a semi-infinite medium. The distribution of residence times is given by

$$g(t) = (4\pi D_p t/\tau)^{-1/2} t^{-1} \exp\left[-(1 - t/\tau)^2(\tau/4D_p t)\right]. \qquad (4)$$

Here τ is the turnover time or mean residence time and D_p is the dispersion parameter. ($D_p = D/vx$, where D is the dispersion coefficient (square meters per second), v the

TABLE 3. Results for Exponential Model With Sinusoidal Input (Approach 1)

Lysimeter	Amplitude, B, ‰	Mean Residence Time, days	Expected Lag, days	New Water, %	EM τ, days	DM2 τ, days
		First Group				
SL4, pit A	15	12	6	44	15	13
SL7	12	15	7	37		
		Second Group				
SL1, SL5, SL6, SL10	3–4	48–65	8	11–14	70	42
		Third Group				
SL3, SL11, pit 5	2	100	8	7		
SL2, SL8, SL9	<2	>100	8	<7	154	63

B is the peak-to-peak amplitude. Mean residence times from best fit models (EM and DM2) for SL4, SL5 and SL2 are also shown (see text).

mean transit velocity of water in the system (meters per second) and x the length of the lines of flow (meters)). The dispersion model is flexible because it permits wide variation of residence time distributions. Consequently, it has been found to be an effective simulator for a wide variety of hydrological systems [*Zuber*, 1986]. However, our experimental system does not correspond well to the conditions for which the solution was derived and it was found to produce unreasonable values of the parameters when it was applied to simulate the SL4 data.

This failure led to a search for a system response function that would produce more reasonable parameters and a better fit to the data. The second dispersion model (DM2) was obtained by combining the C_{IFF} and C_{IRR} solutions of *Kreft and Zuber* [1978]. Thus

$$g(t) = (16\pi D_p)^{-1/2}[(t/\tau)^{1/2} + (\tau/t)^{1/2}]t^{-1} \cdot \exp[-(1 - t/\tau)^2(\tau/4D_p t)] \quad (5)$$

As will be seen, this gave better results, particularly for simulating the SL4 data. The physical meaning of this solution will be discussed elsewhere, but may be thought of as combining two flow systems with different boundary conditions [*Kreft and Zuber*, 1978]: the C_{IFF} part in which tracer is injected and sampled in proportion to the flow, and the C_{IRR} part in which tracer is injected and sampled instantaneously in water volumes.

To include a weighting of the input data in the simulations, equation (2) was modified as follows:

$$\delta_{out}(t) = \frac{\int_0^\infty g(t')w(t - t')\delta_{in}(t - t')\, dt'}{\int_0^\infty g(t')w(t - t')\, dt'} \quad (6)$$

where the weighting is expressed by the function $w(t)$. The appropriate factor with which to weight the rainfall depends on the nature of the water flow to the samplers. If the flow is dominated by displacement flow, the rainfall δ values should be weighted by the amounts of rainfall (fully weighted case) or, more correctly, by the net rainfall or throughfall incident on the ground. On the other hand, if bypass flow is important and excess water is rapidly removed from the soil, then weighting may not be required at all (unweighted case), or only partially (semiweighted case). In the latter case, rainfall up to 40 mm in each week was included in the weighting and any remainder was assumed to bypass the soil matrix. These cases do not cover all possibilities, but are sufficient to allow the effect of weighting to be investigated.

The quality of fit of the simulations to the experimental data was computed using the χ^2 test in the form

$$\chi^2 = \sum_i \left(\frac{X_i - M_i}{\varepsilon_i}\right)^2 \quad (7)$$

where X_i are simulated values, M_i the measured values and ε_i the measurement error in δD (±1‰). The probability that the simulated and measured δD values agree within experimental error can be determined from χ^2 tables.

First Approach: Exponential Steady State Model With Sinusoidal Input

The δD values of the rainfall varied from −10 to −68‰ during the 14 weeks of sampling (Figure 2). This variation was nearly sinusoidal in character, so it is convenient to use the smoothing observed in the soil water to determine the mean residence time of water in the soil by the method used by *Maloszewski et al.* [1983] and *Pearce et al.* [1986]. The following equations relate the decrease in amplitude of variation of δD to the mean residence time and phase lag [*Maloszewski et al.*, 1983] assuming an exponential flow model:

$$\tau = \omega^{-1}[(A/B)^2 - 1]^{1/2} \quad (8)$$

$$\cos\phi = (\omega^2\tau^2 + 1)^{-1/2} = B/A \quad (9)$$

A and B are the amplitudes of the input and output sine curves, ω the angular frequency of variation and ϕ the phase lag.

For the rainfall, average peak-to-peak amplitude and period of variation are about 36‰ and 34 days respectively (determined by fitting a sine curve to the data). Mean residence times and lag times derived from (8) and (9) for the suction sampler data are given in Table 3. The table also gives the fraction of new water. This is defined as water with residence times less than one week and was computed from

TABLE 4. Calculation of New Water Input for SL4 Using Nonsteady Exponential Models (Approach 2)

Date (1987)	Rainfall Depth, mm	δ_R, ‰	Suction δ_{SLO}, ‰	Lysimeter δ_{SL}, ‰	Mixing Model New Water, %	Mixing Model τ, days	Kalman Filter New Water, %
Sept. 1–4	81	−40.1	−42.0	−41.6	21 ± 70	30	⋯
Sept. 4–9	26	−44.1	−41.6	−42.5	36 ± 56	16	37
Sept. 9–15	74	−54.8	−42.5	−48.0	45 ± 22	12	38
Sept. 15–22	26	−25.0	−48.0	−39.8	36 ± 6	16	38
Sept. 22–29	18	−28.4	−39.8	−33.0	60 ± 13	8	36
Sept. 29 to Oct. 6	44	−10.7	−33.0	−25.5	34 ± 7	17	34
Oct. 6–13	152	−34.0	−25.5	−36.6	130 ± 22	⋯	53
Oct. 13–21	54	−68.1	−36.6	−45.8	29 ± 4	29	30
Oct. 21–27	26	−46.0	−45.8	−44.3	−750 ± ∞	⋯	30
Oct. 27 to Nov. 3	62	−39.6	−44.3	−40.4	83 ± 30	4	30
Nov. 3–10	35	−26.7	−40.4	−36.0	32 ± 10	18	30
Nov. 10–17	40	−48.4	−36.0	−37.4	11 ± 11	60	26
Nov. 17–29	107	−56.6	−37.4	−46.2	46 ± 7	11	31
Nov. 29 to Dec. 3	44	−35.9	−46.2	−38.1	79 ± 14	4	35
Dec. 3–9	33	−23.3	−38.1	−33.0	34 ± 9	17	34
Weighted Mean		−41.2			42	13	34

$$g(1) = \int_0^1 g(t')\, dt' \tag{10}$$

The mean residence times vary from 12 days to >100 days, while the lag times predicted are relatively constant at about one week. (Note that these mean residence times are model-dependent; see below.) The responses fall into three groups. The members of the first group are the most responsive and includes SL4, SL7 and pit A throughflow. They have mean residence times of 12–15 days. SL4 and 7 were located at shallow depth immediately below the humic layer and pit A draws from shallow soil in a ridge top location. Both SL7 and pit A are close to the catchment boundary. The members of the second group, including SL1, 5, 6 and 10, show much less variation of δD and have mean water residence times of 50–70 days. They are all set at 400 mm depth and are located throughout the catchment, except in the valley bottom area near the weir. The third group shows the smallest variation of δD and has mean residence times of about 100 days or more. Water from SL3 and SL11 and pit 5 throughflow shows some variation (estimated amplitude of 2‰). These sites are located in midslope hollow positions with relatively deep soils. Samplers SL2, SL8 and SL9 show almost no isotopic variation except for a gradual upward trend. SL2 and SL9 are in generally saturated conditions and all are near the channel in deep soil horizons.

Results from Table 3 can be compared with the throughflow results of *Sklash et al.* [1986], who identified two types of throughflow response in the catchment. In that study, type 1 sites were pits at ridge top and high-elevation locations with ephemeral flows after rainfall. They included pit A (also pits 1, 2 and 3 [see *Sklash et al.*, 1986]) and had 30–40% new water contributions. Our first group can be identified with this type. Type 2 sites of Sklash et al. included pit 5 throughflow and perennial natural seepage, both from deep soil valley sites. These had low new water contributions following rainfall (<10%). The third group of the present work can be identified with this type. Our second group is intermediate between these two types, but closer to the second type. In the Sklash et al. model, streamflow following rainfall was derived predominantly from type 2 sites, together with new water added by direct rainfall on channel and near-channel areas.

Second Approach: Nonsteady Exponential Models

Mixing model. A simple, nonsteady model can be applied assuming mixing between soil water and incoming rainfall. Water from rainfall during the week (δ_R) is added to preexisting soil water, as represented by the previous suction sample (δ_{SLO}), to produce the final soil water δD (δ_{SL}). The fraction of rainfall in the mixture is x. Thus

$$\delta_{SL} = (1 - x)\delta_{SLO} + x\delta_R \tag{11}$$

or

$$x = (\delta_{SL} - \delta_{SLO})/(\delta_R - \delta_{SLO}). \tag{12}$$

Equation (11) can be recognized as the difference equation for an exponential distribution. Since x can vary from sample to sample, the model is nonsteady. Water is considered to drain nearly continuously from the soil so that over time the input of rainfall equals the output of evapotranspiration and drainage.

Values of x derived from (12) for SL4 are given in Table 4, together with estimates of error due to measurement error, and are plotted in Figure 2. Factors expected to cause variation in x are rainfall amount, rainfall timing before soil water sampling and antecedent soil water content. The fraction of new water observed for SL4 varied greatly, ranging from 11 to 130% with an error-weighted average of 42%. This average is very similar to that obtained above (Table 3). Although some of the errors are very high, the wide range of values of x is not entirely due to measurement error. Examination of the most extreme value (130% on October 13) is interesting. In this case, rainfall was particularly heavy during the week (152 mm) with mean δD = −34.0‰ and rainfall at the end of the week was much more negative than that at the beginning (−47.1‰ compared with −24.4‰; see Figure 2). Using a δ_R value of −47.1‰ would give x of 51%; a more reasonable result. Evidently, variation of δ_R (where the change is consistently in one direction) is an important factor affecting x. The other extreme value (11%

TABLE 5. Parameters of Best Fit Models for δD Variations in SL4, SL5 and SL2, With Inputs Either Unweighted, Semiweighted or Fully Weighted by the Amount of Rainfall (Approach 3)

Sampler	Model	Model Parameters D_p	τ, weeks	χ^2	Probability, %	Time to Peak, weeks
			Unweighted			
SL4	EM	···	2.1	117	<0.1	0
	DM1	>12	>20	69	<0.1	0.3
	DM2	2	1.8	62	<0.1	0.16
SL5	EM	···	10	71	<0.1	0
	DM1	0.3	8	23	4	3.6
	DM2	0.2	6	22	5	3.9
SL2	EM	···	22	44	<0.1	0
	DM1	0.2	11	9.7	70	6.2
	DM2	0.18	9	9.6	70	6.1
			Semiweighted			
SL4	EM	···	2.2	144	<0.1	0
	DM2	2	1.7	88	<0.1	0.15
SL5	EM	···	8	91	<0.1	0
	DM2	0.2	6	38	<0.1	3.9
SL2	EM	···	23	52	<0.1	0
	DM2	0.14	8	16	25	5.9
			Fully Weighted			
SL4	EM	···	1.5	230	<0.1	0
	DM2	3	1.5	140	<0.1	0.09
SL5	EM	···	9	93	<0.1	0
	DM2	0.25	6	48	<0.1	3.5
SL2	EM	···	36	61	<0.1	0
	DM2	0.16	8	27	1	5.7

The quality of fit is evaluated using the χ^2 estimator, which gives the probability that the simulated and measured δD values agree within measurement error. The time to peak of the model response functions is calculated from model parameters.

on November 17) was a case where less rain fell and the high δD of the previous week's rain may have had a delayed effect on the soil water.

Mean residence times for each week for SL4 are also given in Table 3. These were calculated from

$$\tau = -1/\ln(1 - x) \quad \text{weeks} \tag{13}$$

The weighted mean residence time is 13 days.

The method has shown similar results for SL7, but is less applicable to other suction lysimeters, because these show much smaller δD variations and therefore larger relative error.

Kalman filtering. The Kalman filtering technique also allows model parameters to vary, but smooths the parameter estimates by including the influence of weeks before the current week. The influence of previous weeks is allowed to decrease exponentially with time before the present. This is physically reasonable (and useful to reduce the short-term effects found in the previous section) for systems with mean residence times longer than about 7 days. (A description of the approach applied here is given by *Minchin and Troughton* [1980] for a somewhat different application. Kalman filtering was applied to a similar hydrological system by *Turner et al.* [1987].)

Applying the technique to the SL4 data gives the new water fractions given in Table 4 based on the exponential model. Apart from particularly high and low values on October 13 and November 17 respectively (discussed above), there is a gradual decrease in x until about November 29 followed by a small rise. The mean value of x was 34%. It is logical to identify the decreasing value of x with increasing average wetness in the soil, because new water will be more strongly diluted in wet conditions. In addition, the period from September 4 to November 11 was somewhat wetter than average (740 mm of rainfall against the expected average of 610 mm). In this approach, the difference equation

$$\delta_{SL} = -A_1\delta_{SLO} + B_0\delta_R \tag{14}$$

was fitted to the data with the above constraint on the value of B_0 (= x). The gain of the system ($B_0 - A_1$), which appears to be related to change of catchment wetness, varied from 0.91 (December 3) to 1.26 (October 13) with an average of 1.00. Hence the system (SL4) was steady state in the overall period, but unsteady on shorter time scales. The mean residence time is given by

$$\tau = -1/\ln(-A_1) \quad \text{weeks} \tag{15}$$

and was found to vary from 12 to 25 days with an overall average of 15 days.

Third Approach: Lumped Parameter Models Assessed by Goodness of Fit

A variety of models and different rainfall weightings were investigated to match input to outputs. The exponential model (EM) and the dispersion models (DM1 and DM2) gave the most satisfactory fits to the data. Among rejected models were the piston flow model and combinations with the exponential and dispersion models. (Piston flow occurs where there is negligible mixing between waters of different residence times.) Both the piston flow and exponential–piston flow models give narrow and rather unrealistic residence time distributions. The dispersion–piston flow model is more flexible, but gave little improvement over the disper-

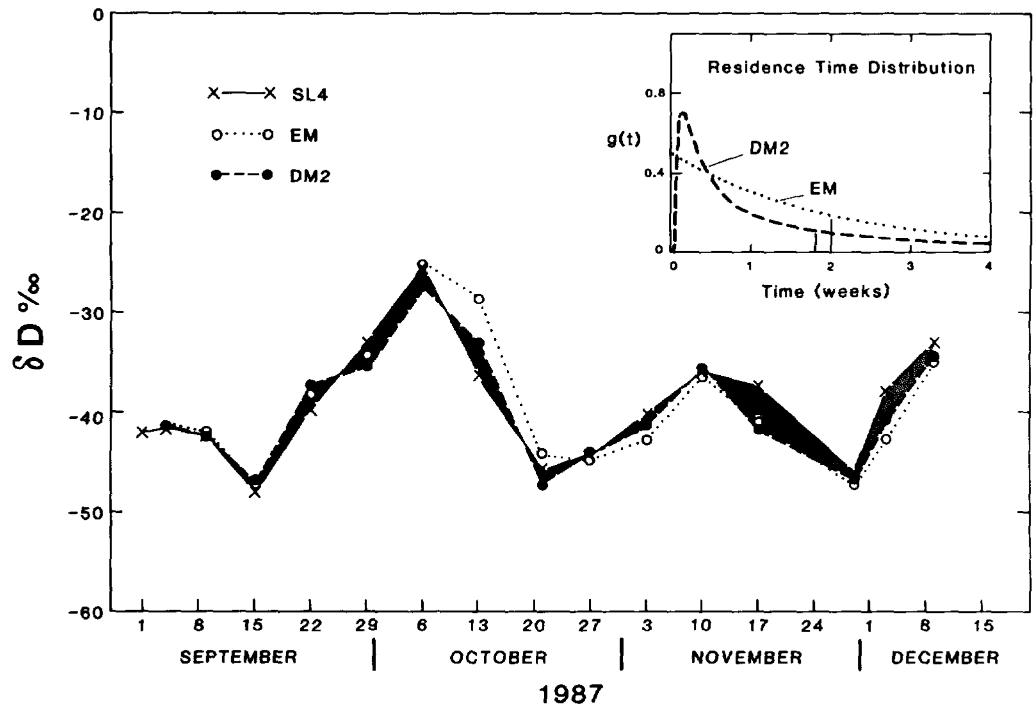

Fig. 4. Comparison of SL4 deuterium concentrations with model simulations. The residence time distributions of the models are shown in the inset (EM, exponential model; DM2, dispersion model 2).

sion model. (See *Zuber* [1986] for the derivation and description of these models).

Using rainfall δD as input, simulations were carried out for δD data from SL4, SL5 and SL2. These samplers constitute a representative sample of the responses. SL4 is representative of shallow depths in the mineral soil at midslope and upper slope locations. SL5 is at greater depth (400 mm) at the midslope location. SL2 is at depth (800 mm) near the stream. These samplers had the longest continuous δD records. The parameters of the models which gave the best fits are given in Table 5. The simulated and measured data are compared in Figures 4 and 5.

All three simulations for SL4 using unweighted input data agree quite well with the measured values from simple inspection of the plot (Figure 4; the simulation for DM1 is not shown, but is similar to that for DM2). The EM has the highest χ^2 (Table 5) indicating the poorest fit, while the DM2 fits better than the DM1. The best fit EM parameter ($\tau = 2.1$ weeks) agrees approximately with the values obtained with approaches 1 and 2 (Tables 3 and 4). The parameters obtained with the optimum DM1 model ($\tau > 20$, $D_p > 12$) are extreme and unrealistic; D_p is not expected to be much greater than 2 in natural systems. The extreme parameters appear to be the result of trying to fit an inappropriate flow model to the data. In contrast, the optimum DM2 parameters have reasonable values and produce a better fit to the data. The mean residence time (τ) is slightly smaller than that for the EM. These parameters indicate that the DM2 distribution ($g(t)$) has an appropriate form for matching the SL4 data. (Note, however, that the actual distributions obtained by matching the DM1 and DM2 to the SL4 data are very similar, in spite of the extreme values of the DM1 parameters.)

The χ^2 values (for $\varepsilon_i = \pm1‰$) are quite large and show that the differences between the simulated and measured data cannot be explained solely by measurement error in δD; the probability of this is less than 0.1%. However, the analytical error is not the total error; some additional error arises from difficulty in determining the appropriate δD values of the rainfall to use as input. (This is illustrated by the October 13 and November 17 simulated values being the most different from the measured values (Figure 4), which is due to change of the δD value of rainfall during the week, as discussed above.) Systematic errors due to evaporation from soil and throughfall are considered to be negligible, as discussed below. If the total error is taken to be $\varepsilon_i = \pm2‰$, the DM2 simulation is found to be not significantly different from the measured data (probability 25%), while the EM is still significantly different (probability 1%).

Simulations were also carried our using different weightings of the input data with the EM and DM2 models (Table 5). The best fitting semiweighted (weighted by rainfall up to 40 mm in each week) and fully weighted (weighted by rainfall amount) input models gave considerably worse fits for SL4 than the unweighted input models. For the EM, χ^2 was 144 and 230 for the semiweighted and fully weighted inputs respectively, while for the DM2 they were 88 and 140. This was somewhat surprising, but on reflection indicates that bypass flow in larger pores and cracks in the soil is important for the SL4 sampler location. Maimai soils are normally within 90% of saturation at most locations [*McDonnell*, 1990]; hence soil matrix adjacent to pores rapidly become saturated during storm events. Consequently, only a small proportion of each rainfall contributes to the soil matrix water, although mixing or exchange of water can still occur.

The system response functions (or residence time distributions) obtained for the EM and DM2 models in the unweighted input case are illustrated in Figure 4 (inset). The DM2 distribution has a peak close to zero (at 0.16 weeks;

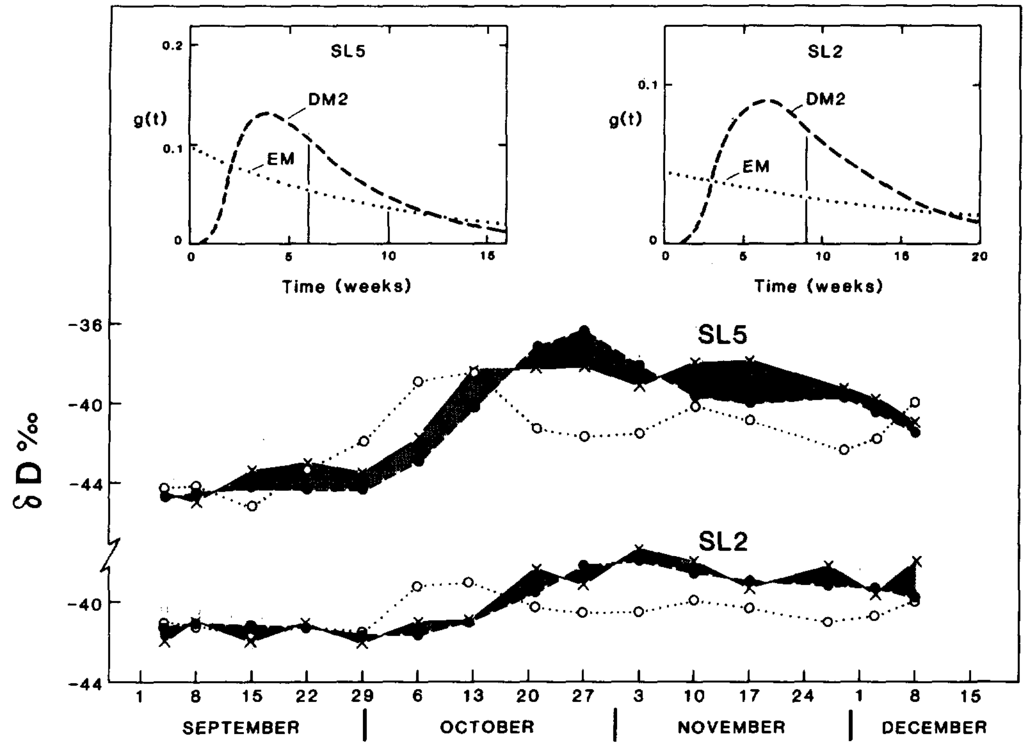

Fig. 5. Comparison of SL5 and SL2 deuterium concentration with model simulations. The residence time distributions of the models are shown in the insets.

Table 5) and a majority (70%) of the water has residence times of 0–5 weeks, 92% for the EM. New water (0–1 week) contributes 38% of the total for both models. The shape of the EM distribution is quite similar to that of the DM2, but the DM2 contains more very young and very old water.

For SL5, the best simulations are obtained with the DMs and unweighted inputs (Table 5). There is only a small difference in quality of fit between the DM1 and DM2, and the parameters obtained are similar. Apparently, the response functions for these models are almost equally appropriate, although the DM2 fit is still slightly better. The EM produces a much worse fit, and longer mean residence time (τ = 10 weeks). This agrees with the earlier value for SL5 if the amplitude of variation is 3‰ (τ = 65 days, see Table 3). Figure 5 illustrates the poor quality of the EM fit. There is a 5% probability that the differences between the DM simulations and SL5 data result from measurement error, whereas it is much less than 0.1% for the EM.

The different input weightings again yielded much worse fits (Table 5). As before, the higher the weighting the worse the fit. The poorer fits of the weighted cases again indicate the importance of bypass flow at this location.

The response functions for the unweighted case are given in Figure 5 (inset). The DM1 and DM2 have similar peak residence times (~4 weeks) and less than 1% new water. Seventy percent of the water has residence time between 2 and 9 weeks. Comparison of the response functions for the EM and DM2 suggests that the reason for the poor fit of the EM is that it includes too much very young water (10% of new water). In compensating for this, optimization causes too much old water to be included. The combination of young and old water does not exhibit the same response as the intermediate age water of the DM2.

Simulations for SL2 are given in Table 5. The DM1 and DM2 give similar results. The unweighted DM2 is much better than the semiweighted and fully weighted DM2 simulations. All of these are better than the best EM, however, which is the unweighted EM. It is concluded that a bypass mechanism is important for this near-stream location.

The mean residence times obtained with the DMs are very much shorter than those obtained with the EM. According to the χ^2 test, the unweighted DM is not significantly different from the measured data. The δD variation of SL2 is strongly damped, so it is easier to achieve small χ^2 values, since the measurement error is large compared to the variation. Considering this, the EM fits very poorly indeed. The simulations for the unweighted cases are illustrated in Figure 5. From the DM2 response function, we see that the peak residence time is 6 weeks and the majority of water reaching the sampler has residence time between 3 and 13 weeks (70%). New water is excluded. The unweighted EM curve is shown for comparison. Its response function has mean residence time of 22 weeks and includes 4% new water, which considering the poor match to the data, is expected to be incorrect. The 22 weeks agrees with the previous estimate of $\tau > 100$ days (Table 3).

DISCUSSION

Isotope Fractionation of Soil Water

Our analysis has assumed that deuterium is a conservative tracer in soil water and that changes in deuterium concentrations are brought about only by mixing of waters of different residence times. We briefly discuss three possible causes of deuterium fractionation and why we consider them to be of minor significance in the Maimai catchment. All would cause enrichment in deuterium. They are evaporation of throughfall, evapotranspiration and evaporation in the suction cup.

Evaporation of throughfall or interception loss can cause enrichment in deuterium. Interception loss is significant at Maimai (~25% of gross rainfall), and is expected to be greatest in summer. The degree of deuterium enrichment depends mainly on the relative humidity, which is generally close to 100% during rainfall. Measurements have shown only slight deuterium enrichment due to evaporation of throughfall in a pine forest at Canterbury where interception loss was 30% [*Pearce et al.*, 1986]; the more humid environment at Maimai should lead to less enrichment.

Experimental studies have shown that no detectable isotopic fractionation of soil water occurs during plant transpiration [e.g., *Zimmerman et al.*, 1967] and that negligible evaporative enrichment of soil water is to be expected in wet conditions [e.g., *Darling and Bath*, 1988]. The nonfractionating nature of capillary flow is thought to be the reason for the lack of isotopic fractionation.

Extraction of moisture from the soil into the suction samples exposes the water to low pressure, but only until the lysimeter is filled. After this short period, the water cannot evaporate. Measurements by *Swistock et al.* [1989] confirmed that the suction lysimeter does not have a significant effect on soil water δD. They found no significant difference between pan and suction cup ^{18}O values, based on 10 concurrent lysimeter samples.

These processes would cause the soil moisture to have a higher deuterium content than the rainfall. The average δD of short residence time group 1 lysimeters (SL4 and SL7) was found to be −39‰ compared to the rainfall mean of −39‰ (rainfall amount-weighted mean is −41‰), showing that any enrichment is slight. Group 2 and 3 lysimeters had mean δD of −40‰. This is good evidence that these deuterium enrichment mechanisms have had negligible effects on the present samples.

Moisture Flow in Maimai Soils

Three approaches to interpreting the deuterium variations in soil water were used. The main advantage of the first approach was that it could be applied to all of the suction samples and pit flow data, while the later approaches are difficult to apply if data are missing. It also enabled comparison to be made with previous work [*Sklash et al.*, 1986] and approaches 2 and 3. Groupings established with approach 1 are model-independent, but the parameters are not. For example, the EM and DM2 gave very different mean residence times for the SL5 and SL2 data (Table 5). Because of the poor fits produced by the EM and the very good fits by the DM2, we conclude that the groupings in Table 3 are valid, but the mean residence times obtained with the DM2 should be used, instead of those with the EM (Table 3). These indicate soil water mean residence times of up to two months in the catchment.

The mixing model (approach 2) revealed large short-term variations in mean residence time from week to week for SL4, although some of this variability results from using the weekly average rainfall δD values as input (as discussed above). A more appropriate choice of δ_R (covering more or less than one week's rainfall) would reduce the variability. The Kalman filter technique allows the mean residence time to vary, but smooths the variation by averaging over previous weeks. The influence of previous weeks is allowed to decrease exponentially with time before the present. The new water percentage (x) shows a gradual decrease to November 29, 1987, which is thought to be in response to wetter than average conditions in the catchment during this time period (Table 4).

Models that produced the best matches to the data were selected in the third approach. The input was weighted by the weekly rainfall to take account of the amount as well as the δD of the rainfall. However, this weighting procedure was found to produce worse fits to the experimental data for all models and types of weightings applied. (Weightings used were total weekly rainfall, rainfall up to 40 mm per week and net rainfall (i.e., throughfall; results not given in Table 5)). In all cases, the weighted simulations were poorer than unweighted simulations, leading to the conclusion that much of the rainfall bypasses the soil matrix. This important conclusion agrees with the hydrometric observations of *Mosley* [1979, 1982] and later workers (see introduction to this paper). However, *Sklash et al.* [1986] have shown that throughflow at all locations on the slopes is dominated by old water following rainstorms (with the proportion of old water increasing downslope). Hence, rainfall not only bypasses the soil matrix, but also mixes with soil water to a considerable degree on short time scales. *McDonnell* [1990] has discussed the processes by which new water incident on the soil is converted to throughflow dominated by old water. In brief, it is thought that saturation of regions surrounding macropores, cracks, etc., cause enhanced conductivity and bypass flow. Thus old water is mobilized with new. Soil matrix not brought to saturation by new/old water in the bypass channels receives water much more slowly by diffusion (capillary flow) and hydrodynamic dispersion.

Of the models tested, the EM gave a reasonable fit to the SL4 data and poor fits to the SL5 and SL2 data, while the dispersion models gave good fits to all three suction samplers. There is a sharp distinction between the DM1 and DM2 results for the SL4 data; the DM2 gives reasonable values of the parameters, while the DM1 does not. This is attributed to the large D_p values required for the fits (corresponding to small Péclet numbers), which indicate greater importance of capillary flow or hydrodynamic dispersion compared to advection in this situation. The DM1 is not appropriate for modeling diffusion (capillary flow). The distinction between the DM1 and DM2 is much less with the soils of SL5 and SL2, because the D_p values are smaller, indicating that advection processes are more important.

These results are interpreted as follows. In the responsive first group (SL4, SL7 and pit A), which are at shallow levels in unsaturated soils, capillary flow from temporarily saturated bypass channels supplies water to the soil matrix to satisfy loss by evapotranspiration and gravity drainage. Travel times peaking at one day, but with a distribution skewed toward longer times, are indicated by the system response function for SL4 (Figure 4, unweighted DM2). Drainage from these soils is slight and throughflow is ephemeral following rainfall (as shown by pit A flows).

Soil at 400 mm at the midslope hollow site (SL5) is subjected to periodic saturation during and after rain events. This causes mixing (hydrodynamic dispersion) with predominantly old water and advection. Capillary flow and evapotranspiration and gravity drainage resume during drying periods. The response function (DM2, Figure 5) indicates a delayed flow peaking at 3.6 weeks, positively skewed. The delay represents the combined effect of various episodes of mixing with preexisting soil water and bypass flow during storm events. If bypass water has the same composition, then the mean residence time indicates a soil water store of 180 mm.

Deep soils near the stream (SL2) are generally saturated with old water. The response function (Figure 5) shows a positively skewed broad peak at 6 weeks, i.e., a delayed flow response caused by many episodes of mixing and bypass flow. A soil water store of 280 mm is indicated.

The big difference between the isotopic responses of group 1 soils and group 2 and 3 soils can now be seen to result from the homogenizing effects of occasional water table developments in the group 2 and 3 soils.

SUMMARY

Measurements of the deuterium content of soil moisture collected from 11 suction cup samplers, two pits and natural flow sites at five different locations in the Maimai M8 catchment for 14 weeks in spring 1987 were compared with the deuterium concentrations in rainfall over the same period.

Suction cups at 400 to 800 mm depths at midslope and slope bottom locations produced isotopically well-mixed waters with relatively slight responses to the strongly varying deuterium concentrations in precipitation. The peak-to-peak amplitudes of deuterium variation ranged from 0 to 4‰ compared to precipitation (36‰). These are subject to periodic perched water table development. In contrast, suction cups at 200 and 300 mm depth and pit A at midslope and upper slope locations yielded waters exhibiting considerable isotopic responses (12–15‰) to precipitation. These are in unsaturated soil.

Three approaches to determining the mean water residence times from the isotopic data were investigated. A steady state exponential model with sinusoidal input allowed three groups of soil water response to be defined. The groupings were consistent with the results of *Sklash et al.* [1986], but covered a greater range of responses. Mean residence times estimated ranged from 12 to more than 100 days, but more accurate values are obtained for the longer times by the dispersion model (DM2) below.

The second approach used nonsteady exponential models. Average mean residence times and new water fractions were similar to those obtained by the first approach, but the new water fractions varied strongly from week to week. These results indicated that steady state models are applicable to the system for the overall time scale investigated.

The third approach tested the ability of different types of models to simulate the soil water δD data using the criterion of goodness of fit. Unweighted exponential and dispersion models gave the best fits. Weighting the input (rainfall δD) partially or fully with the amount of rainfall gave much worse fits, showing that much of the input water bypasses the soil matrix. Bypass flow is dominated by old water, however. The exponential model was not as successful as the dispersion models, but was relatively best for the SL4 data. Of the two dispersion models tested, the DM2 (based on the C_{IRR} and C_{IFF} solutions to the dispersion equation) was clearly superior to the DM1 (C_{IFF} solution) for the SL4 data. This shows the importance of capillary flow as opposed to hydrodynamic dispersion for water flow in the unsaturated SL4 soil matrix. The DM2 advantage was not maintained for the SL5 and SL2 data, and both models gave similar results, showing that advection and hydrodynamic dispersion (mixing) are more important for these occasionally saturated soil locations. Mean residence times estimated using the DM2 were 13 days (SL4), 42 days (SL5) and 63 days (SL2). The nature of soil water flow at these sites was discussed.

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