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Journal of Hydrology 261 (2002) 132–149

Journal of Hydrology

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Evaluation of mean residence time in subsurface waters using oxygen-18 fluctuations during drought conditions in the mid-Appalachians

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Received 20 October 2000; revised 29 November 2001; accepted 25 January 2002

Abstract

Seasonal variations of the stable isotope, oxygen-18 (^{18}O), were used to estimate mean residence times (MRTs) of water in two Valley and Ridge Province watersheds in central Pennsylvania. MRT was estimated by applying ^{18}O input precipitation signatures to response function models that describe flow conditions in the subsurface system. Precipitation ^{18}O is usually seasonally periodic; however, during this study period (March 1998 to June 1999), unusual weather conditions and severe drought caused an abnormal seasonal signature in precipitation ^{18}O. The atypical input precipitation amounts and ^{18}O signatures required that adjustments be made using recharge factors and an extended past input function to represent the varying fraction of input water that contributed to turnover within the watershed during the study period. Oxygen-18 variations were investigated in output waters from tension and zero-tension soil water lysimeters, shallow wells, and streamflow. Soil water ^{18}O signatures were more responsive to precipitation ^{18}O variations than streamflow ^{18}O signatures. Theoretical models based on exponential piston-flow and dispersion flow processes fit data better than did other groundwater age distribution models (i.e. pure piston flow or pure exponential models). Analysis suggested that during drought conditions, larger portions of older water dominated streamflow ^{18}O composition, and that the current year's precipitation ^{18}O signature became more attenuated in the subsurface flow system. MRTs obtained for streamflow at each site were 9.5 and 4.8 months for a 14 and 100 ha watershed, respectively, and soil water MRT at 100 cm depth was on the order of a couple months; indicating a relatively rapid response of shallow groundwater to precipitation.

Keywords: Residence time; Seasonal variation; Stable isotopes; Tracers; Numerical methods; Transfer functions

1. Introduction

The mean residence time (MRT) of shallow groundwater is the average time water spends in the subsurface system before it reaches a designated point along its flow path, such as a watershed outlet or specific soil depth. Knowledge of residence time is important for contaminant transport studies and in examining watershed response to land-use/environmental changes. The MRT of a system can suggest either the potential for groundwater contaminant decay or response time to imposed management

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PII: S0022-1694(02)00006-9

practices or land-use changes. Consequently, MRT plays an important role in controlling the quality of water that drains soils or watersheds.

Stable isotope (^{18}O or ^{2}H) seasonal variations in precipitation and subsurface waters have been used in recent years to estimate the MRT of water exiting a watershed (DeWalle et al., 1997; Maloszewski et al., 1983; Maloszewski et al., 1992; McDonnell et al., 1999; Turner et al., 1987; Vitvar and Balderer, 1997). Stable isotopes are conservative, naturally occurring tracers that are applied by precipitation events and are typically distinct isotopically, making them reliable tracers of subsurface flow processes (Kendall and Caldwell, 1998). MRT estimation takes advantage of isotopically distinct water in precipitation that propagates in a known pattern over time into subsurface systems, and exits with a new isotope signature and pattern dependent on subsurface flow paths and hydrodynamic dispersion. Oxygen and hydrogen stable isotopes are useful for approximating stream and shallow groundwater residence time because they are not contaminated by exchange with the atmosphere (as opposed to CFCs and $^{3}H/^{3}He$) and sample collection and storage is relatively simple and inexpensive. Furthermore, stream water in small watersheds typically has MRTs that are <5 years old (Kendall and McDonnell, 1998), which are within the range of MRT interpretation using ^{18}O and ^{2}H (Coplen, 1993), given there are detectable variations resulting from precipitation isotope contents.

Most MRT estimation methods are based on models presented by Maloszewski and Zuber (1982); these range from simple sine-wave and isotope damping analysis of stable isotope data (Burns and McDonnell, 1998; DeWalle et al., 1997; Frederickson and Criss, 1999; Kubota, 2000; Maloszewski et al., 1983; Soulsby et al., 2000) to more mathematically complex approaches based on multi-parameter response function models (Amin and Campana, 1996; Haitjema, 1995), power spectra (Kirchner et al., 2000), direct simulation (Etcheverry and Perrochet, 2000; Goode, 1996), and stochastic–mechanistic models (Simic and Destouni, 1999). In this study, a lumped-parameter approach using ^{18}O input signatures and response function models as presented in Maloszewski and Zuber (1982, 1996) was employed to estimate MRT.

The response function models define the theoretical residence time distributions of shallow groundwater flow that result from flow path distributions in the subsurface system. Many models have been used to investigate MRTs of groundwater systems (Amin and Campana, 1996; Cook and Böhlke, 1999; Maloszewski and Zuber, 1982); however, it is uncertain which model (i.e. residence time distribution) and characteristic residence times best represent shallow groundwater flow conditions in small watersheds of the mid-Appalachian region. In addition, more information is needed about the subsurface contact time in small watersheds (10–100 ha) to make predictions about stream water chemical changes from land-use and environmental change.

The overall objective of this study was to determine the MRT of shallow groundwater in two watersheds in central Pennsylvania using models incorporating ^{18}O fluctuations in input precipitation and throughfall, and output soil water, streamflow, and shallow well water. More specifically, the study was designed to determine the types of response function models best suited for estimating MRT when low soil moisture conditions exist, such as during drought conditions. Model types tested in this study are the piston-flow (PF) model, the dispersion model (DM), the linear reservoir or exponential model (EM), and the combined exponential PF model.

1.1. Model theory

For systems with steady flow and the conservative isotopic tracer, ^{18}O, the output isotopic tracer can be related to the input tracer by the convolution integral (Maloszewski and Zuber, 1982):

$$\delta(t) = \int_{-\infty}^{t} \delta_{\mathrm{in}}(t')g(t-t')\mathrm{d}t', \quad (1)$$

where $\delta(t)$ is the output ^{18}O signature, t', an integration variable that describes the entry time to the system, t, the calendar time, δ_{in}, the input ^{18}O signature to the system (i.e. input function), and $g(t-t')$ is the residence time distribution or system response function, which is the travel time probability distribution for tracer molecules in the system.

A conservative tracer's concentration in groundwater is affected by the transport along a distribution of subsurface flow paths and subsequent mixing in the outflow zone (i.e. well or stream). The model types are represented in Eq. (1) by the form of the system response function $g(t)$. The major model types tested as described in Maloszewski and Zuber (1982, 1996) are given below as residence time distribution functions:

Piston-flow (PFM)

$$g(t) = \delta(t - \tau) \tag{2}$$

Exponential (EM)

$$g(t) = \frac{1}{\tau}\exp\left(\frac{-t}{\tau}\right) \tag{3}$$

Dispersion (DM)

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

Exponential-piston-flow (EPM)

$$\begin{aligned} g(t) &= \frac{\eta}{\tau}\exp\left(-\frac{\eta t}{\tau} + \eta - 1\right) \quad \text{for } t \geq \tau(1 - \eta^{-1}), \\ g(t) &= 0 \quad \text{for } t < \tau(1 - \eta^{-1}) \end{aligned} \tag{5}$$

where the main model parameter (τ) is the MRT of the system. The dispersion parameter, $D_p = (D/vx)$, is used as a fitting parameter (Maloszewski and Zuber, 1998) in Eq. (4); however, the physical meaning can be interpreted in terms of transport processes (i.e. geomorphological dispersion, from Rinaldo et al. (1991) and distribution of flow path lengths within the subsurface system). Another fitting parameter, η, is included in Eq. (5), which equals the total volume of water divided by the exponential flow volume. Thus, when $\eta = 1$, the model is equal to the EM and for $\eta \rightarrow \infty$, the model approaches a PFM. The exponential-piston flow model (EPM) (Eq. (5)) is typically used in confined groundwater systems that have isochrones nearly perpendicular to flow paths, which are more likely to yield discharge with a peak in the residence time distribution (Cook and Böhlke, 1999). The resulting residence time distribution from the EPM lacks contribution from the very young water flow paths, which could represent flow paths in an unconfined system (e.g. recharge area) that change to piston flow conditions in a confined system (Maloszewski and Zuber, 1993). The exponential portion of the EPM (Eq. (3)) is similar to the completely mixed assumption of the surface reservoir where the outflow is linearly related to the average or well-mixed behavior of the system (Duffy and Gelhar, 1985; Zuber, 1986). Flow paths of different lengths ranging from zero to infinity with no mixing between flow paths can also characterize the exponential distribution of residence times. Recent discussion on the use of lumped parameter models for interpreting tracer data and residence time was given in Maloszewski and Zuber (1993, 1998) and Amin and Campana (1998).

1.2. Input functions

The input function used in the model (Eq. (1)) must be determined from the pattern of ^{18}O in precipitation adjusted to represent water that contributes to turnover within the watershed (i.e. recharge). Amount-weighted precipitation ^{18}O is typically adjusted by a factor (α) that equals the ratio of the amount of summer infiltration to winter infiltration. The theory for determining input functions that include α is given in Grabczak et al. (1984), Bergmann et al. (1986), and Maloszewski et al. (1992) and is calculated as follows:

$$\delta_{in}(t) = \frac{N\alpha_i P_i}{\sum_{i=1}^{N}\alpha_i P_i}(\delta_i - \delta_{GW}) + \delta_{GW}, \tag{6}$$

where N is the number of time periods for which precipitation was collected (only valid for the complete hydrologic period), P_i and δ_i, the precipitation amount (mm) and isotope composition (‰) for each sample period, and δ_{GW} is the mean isotope composition of local groundwater originating from recent precipitation. The equation is based on the assumption that δ_{GW} must be equal to that of recharge water (Vitvar, 1998). The recharge factor (α) essentially adjusts the precipitation amount to represent the proportion of water that becomes recharge (e.g. $\alpha = 0$ means that recharge does not occur and $\alpha = 1$ indicates that all water is recharged). Instead of only applying a

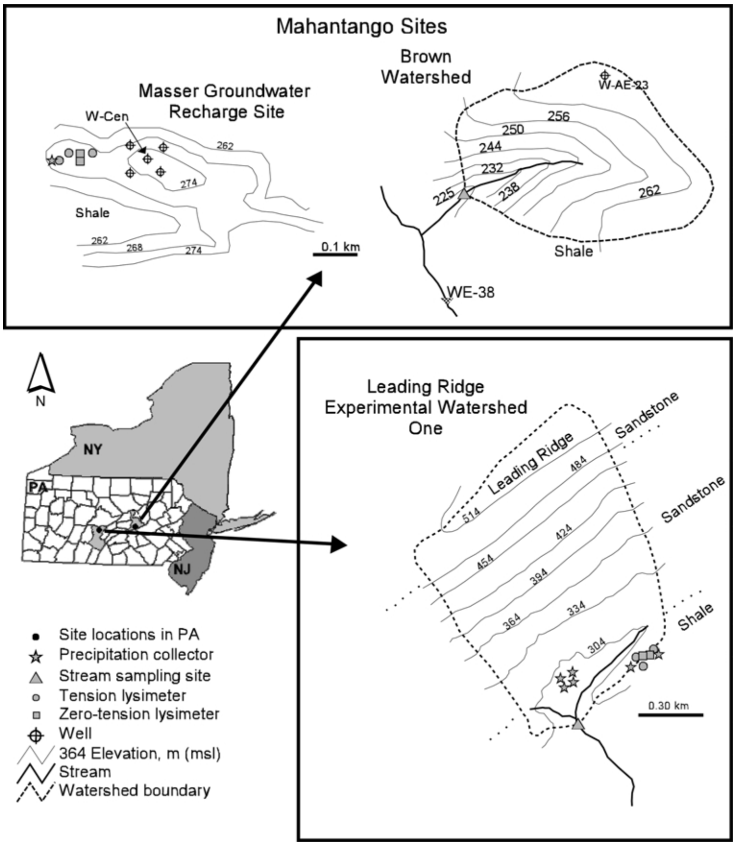

Fig. 1. Location and field instrumentation map of the Mahantango (Masser and Brown sites) and Leading Ridge study sites in central Pennsylvania.

summer/winter recharge factor as calculated by the Grabczak et al. (1984) method, a factor that varies due to evapotranspiration and water availability was also adopted due to the drought conditions affecting the study. During drought conditions, the summer/winter assumption of recharge was no longer valid; thus, a more realistic adjustment was used to represent recharge. A sinusoidal function used by Duffy and Cusumano (1998) was used to represent a varying recharge factor that corresponded to times of active recharge when soil water was collected in zero-tension lysimeters:

$$\alpha_i = a_1 \cos^{a_2}(\omega t + \phi) + a_3, \tag{7}$$

where a_1 and a_3 are positive constants, a_2, a positive whole number (i.e. $0, 1, 2, 3, \ldots$), ϕ, the phase lag in radians between precipitation and recharge, t, the calendar time, and ω is the angular frequency. By manually changing the parameters in Eq. (7) to mimic the patterns of soil water movement, a more realistically shaped recharge factor was established and used as opposed to the summer/winter recharge factor, which was not valid longer. Substituting α from Eq. (7) into Eq. (6) yields an input function that is volumetrically weighted and adjusted to represent water that contributes to turnover in the watershed. An alternative approach would be to physically model recharge (e.g. with a soil water balance model, which requires additional parameters for soil properties and evapotranspiration) to develop recharge factors (Vitvar, 1998). This was avoided to reduce model complexity associated with larger parameter sets, since the residence time models are intended to be simple lumped-parameter models with one or two parameters.

2. Site descriptions

The study sites located in central Pennsylvania represent two major systems in the Valley and Ridge Physiographic Province within the mid-Appalachian region. Leading Ridge is a typical forested sandstone ridge system, while Mahantango Creek is characteristic of agricultural hill-land watersheds in the Susquehanna River Basin (Gburek and Sharpley, 1998). The general climate in central Pennsylvania is characteristic of the humid northeastern continental type. Mean annual precipitation at Leading Ridge is about 1130 mm (Lynch and Corbett, 1989), while in the Mahantango region, mean annual precipitation is approximately 1090 mm (Gburek and Folmar, 1999a). Historically, at both study sites, approximately 60% of the annual precipitation has been lost to evapotranspiration (Gburek, 1977; Lynch and Corbett, 1989).

The Leading Ridge (LR) site is the Leading Ridge Experimental Watershed One, a 122.7-ha watershed in northern Huntington County (Fig. 1). The watershed is completely forested with elevation varying from 265 to 500 m above m.s.l. (Lynch and Corbett, 1989). The geology underlying the upper slopes of LR is Tuscarora quartzite and sandstone, middle slopes are underlain by Castanea sandstone, and the lower slopes are underlain by the Rose Hill Shale Formation (Lynch and Corbett, 1989). The soils on LR are Utisols and Inceptisols, which are fine to loamy-skeletal mixed mesic soils. The Leading Ridge One watershed is 100% forested with a predominantly oak (*Quercus* spp.) overstory.

The Brown watershed (BW) and the Masser groundwater Recharge Facility at Mahantango Creek are two agricultural facilities managed and operated by the USDA-ARS (Gburek, 1977) and are collectively considered the Mahantango study site in this paper. Brown watershed is a subcatchment within the Mahantango Creek Watershed (Gburek, 1977) with an area of 14 ha and varying in elevation from about 225 to 265 m above m.s.l. The geology of the watershed is dominated by the Trimmer's Rock Formation with some outcropping of the Irish Valley Member of the Catskill Formation in the northeastern portion of the watershed (Urban, 1977). Both these formations are predominantly shale. The soils on BW are the Hartleton (Typic Hapludult) and Berks (Typic Dystrochrept) channery silt loams (Pionke et al., 1996). This watershed is nearly all cropped (97%) with corn, alfalfa, and barley.

The Masser site is an intensively instrumented groundwater recharge research facility located on a well-defined topographic knoll approximately 1 km from Brown watershed (Fig. 1). This site has been recently described in detail by Gburek and Folmer (1999b). The underlying geology is the Catskill Formation, which is mostly shale. Residual soils are predominantly Calvin shaley silt loam and the Hartleton channery silt loam (both Typic Hapludults). The site vegetation is typically mowed grass pasture and corn.

Hydrologic conditions during this study (March 1998 to June 1999) ranged from normal to severe drought based on the Palmer Hydrologic Drought Index or PHDI (Karl, 1986; Guttman, 1991). Mild (PHDI $= -1.0$) to extreme (PHDI $= -4.0$) drought conditions were predominant during the study from September 1998 to June 1999 (about 60% of the total study period) (National Climate Data Center, 1999). Approximately 50% of the total precipitation measured during the study fell in the first 5 months (16 March 1998 to mid-August 1998) of data collection, while the remaining 50% fell in the latter 10-month period. Total precipitation measured during the 15-month study period was 1180 and 1205 mm, while estimated evapotranspiration was 62 and 68% of precipitation for Leading Ridge and Masser, respectively, based on simple water balances at these sites (McGuire, 1999).

3. Methods

3.1. Data collection

Water samples of precipitation (or throughfall), soil water, shallow well water, and streamflow were collected at each site (Leading Ridge and Mahantango) at approximately biweekly intervals from March 16, 1998 to June 30, 1999. Soil water was collected at 100 cm depth (below the frost zone and above the water table) using two different devices—zero-tension and tension lysimeters. Leading Ridge zero-tension lysimeters consisted of two 930 cm^2 polyethylene trays filled with excavated soil and installed horizontally in the side wall of a soil pit. Mahantango zero-tension lysimeters were two steel 76 cm diameter (4540 cm^2) cylinders that were bottom-sealed after installation with a hydraulic hammer (Gburek and Folmar, 1999b). A composite sample from three ceramic porous cup tension lysimeters was collected at each site from water that accumulated between biweekly visits. Streamflow samples were collected by hand during non-storm conditions and continuous flow records were maintained at each site. Shallow groundwater samples were collected from the water level surface in two wells at Mahantango, one located at the Masser site (W-Cen) (mean water level depth = 14.50 m; total well depth = 46 m) and one located on Brown Watershed (W-AE23) (mean water level depth = 8.56 m; total well depth = 30 m) (Fig. 1). The well boreholes were cased to approximately 5 m or through the weathered bedrock zone, and then the remainder of each borehole was left open (i.e. no well screening).

3.2. Oxygen-18 analysis

The ^{18}O composition of all water samples (289 samples total) was analyzed by mass spectrometry (Epstein and Mayeda, 1953) at the Stable Isotope Laboratory, Southern Methodist University, Dallas, Texas. The ^{18}O content was reported in per mil (‰) units relative to Vienna Standard Mean Ocean Water (VSMOW). The analytical precision of $\delta^{18}O$ results was 0.11‰ (1 standard deviation) based on 24 blind duplicate pairs.

3.3. Input functions and modeling

Two input functions were constructed using the measured $\delta^{18}O$ and precipitation amounts at each site during the study period. An additional 20 months of $\delta^{18}O$ data prior to the study period were estimated using sine-wave regression equations from DeWalle et al. (1997) and Deines et al. (1990). Other methods of reconstructing past $\delta^{18}O$ in precipitation were not as effective, such as regression models with average temperature (Burgman et al., 1987) and observed precipitation amounts. The precipitation amounts for the extended $\delta^{18}O$ data were obtained from the State College weather station (approximately 21 km from Leading Ridge and 160 km from Mahantango). A longer time series of input data was necessary to properly model MRT for groundwater systems, which typically can have MRTs greater than or equal to the length of our study (15 months). Summer/winter recharge factors were determined by the Grabczak et al. (1984) method for the input data prior to our 15 months of observations, and Eq. (7) was used to determine time-varying recharge factors that corresponded to lysimeter outflow during the study period. The time-varying recharge factors (Eq. (7)) applied only during the study period enabled more accurate representation of recharge during the drought conditions. The input function for each site (Leading Ridge and Mahantango) was used to model all output waters that corresponded to that study site.

After the input functions were prepared, model simulations were determined using the basic forms of Eqs. (1)–(5) to minimize the following least-squares statistic (Maloszewski and Zuber, 1996) in an unconstrained non-linear optimization routine (Lagarias et al., 1998):

$$\Sigma = \frac{\left[\sum_{i=1}^{n}(O_i - X_i)^2\right]^{1/2}}{n}, \tag{8}$$

where O_i are the observed values ($\delta^{18}O$‰), and X_i are the simulated values ($\delta^{18}O$‰). The model produces a simulated output and Σ value for a specified input function [$\delta_{in}(t)$]. In addition to the fitting statistic, Σ, other error and evaluation measures were computed such as the modified index of agreement, coefficient of efficiency, and square root of the mean square error (RMSE). The modified index of agreement (d_1) is a robust goodness-of-fit measure that ranges from 0 to 1, where higher values indicate better agreement (Legates and McCabe, 1999). The coefficient of efficiency (E), as defined by Nash and Sutcliffe (1970), has been widely used in rainfall–runoff modeling. It ranges from $-\infty$ to 1, where higher values indicate better agreement. A negative value of E

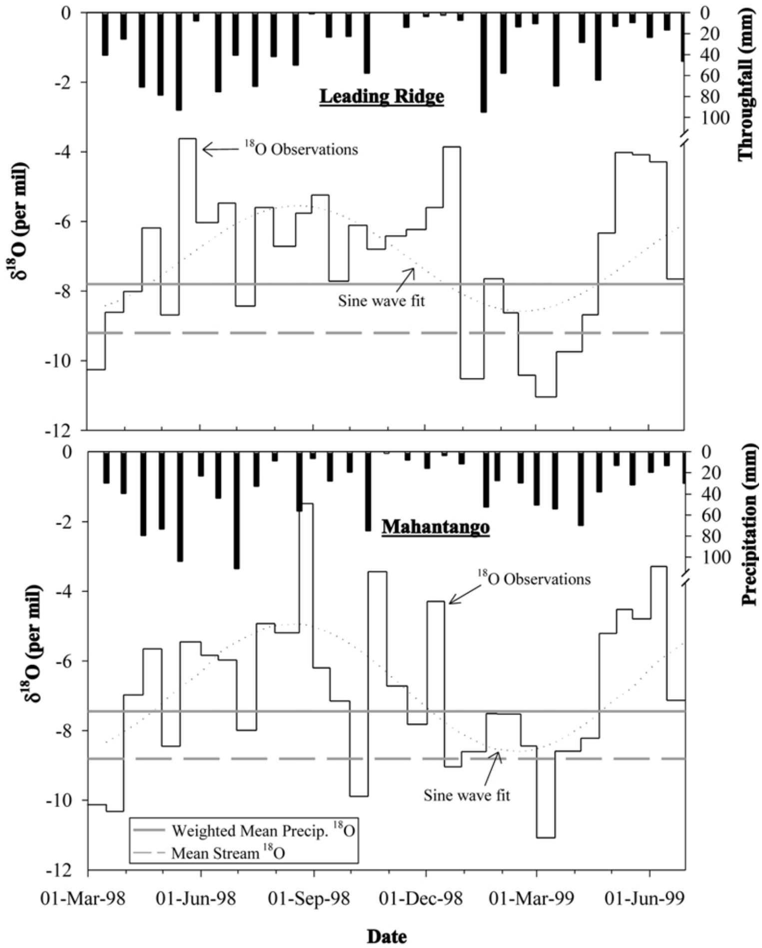

Fig. 2. Precipitation and throughfall δ^{18}O collected at the Mahantango and Leading Ridge sites, respectively. The solid black line represents the measured δ^{18}O from collected samples over biweekly periods (period length is shown by length of the horizontal bar). The dotted line depicts the seasonal trend of ^{18}O variation, and the solid and dashed gray lines show the weighted mean precipitation (or throughfall) and mean stream ^{18}O composition, respectively.

indicates that the observed mean is a better predictor than the model simulation. Both the fitting statistic (Σ) and RMSE quantify the simulation error in per mil (‰) units.

Eq. (1) was used to predict temporal δ^{18}O patterns in the output soil water, shallow well water, and streamflow from the amount-weighted and recharge adjusted input functions for various assumed model types (piston, exponential, and dispersion conditions) and parameters (τ, η, and D/vx).

4. Results

4.1. Isotopic characterization of precipitation and throughfall

The amounts and isotopic signatures of precipitation at the Mahantango site (MS), and throughfall at Leading Ridge (LR) are shown in Fig. 2. Isotopic compositions did not significantly differ between the two sites (paired *t*-test for sample periods, $p = 0.362$). Sine-wave regression models (DeWalle et al., 1997)

Table 1
Sine-wave regression models ($\delta^{18}O = \beta_0 + A[\cos(\omega t - \phi)]$, β_0 = mean annual sine-wave $\delta^{18}O$ value, A = amplitude, ω = radial frequency constant ($2\pi/365$ radians d^{-1}), t = time, and ϕ is the phase lag) for precipitation, throughfall, soil water, stream flow, and groundwater well $\delta^{18}O$ data

Water type/site	β_0 (‰)	Amplitude (‰)	Phase lag[a] (days)	N	P-value	R^2	RMSE (‰)
Mahantango sites							
Masser precipitation	− 6.77	1.84	43.4	32	0.004	0.312	1.919
Tension lysimeters	− 8.85	0.97	65.8	21	0.493	0.076	1.308
Zero-tension lysimeters	− 6.67	3.07	86.5	15	0.232	0.216	1.614
Masser well (W-Cen)	− 8.97	0.14	80.1	32	0.011	0.268	0.167
Brown well (W-AE23)	− 8.69	0.03	88.9	32	0.62	0.032	0.133
Brown stream (FE38-1)	− 8.81	0.21	61.9	32	< 0.000	0.440	0.176
Leading Ridge							
Leading Ridge throughfall	− 7.06	1.52	48.6	32	0.018	0.241	1.888
Tension lysimeters	− 8.29	2.07	77.3	20	0.026	0.349	1.076
Zero-tension lysimeters	− 0.35	9.90	82.7	8	0.219	0.455	1.596
Leading Ridge 1 stream (LR1)	− 9.20	0.52	85.6	32	< 0.000	0.461	0.407

[a] Phase lag is defined as days from 1/1/98, which is the time of annual peak ^{18}O, N is the number of observations, P-value is the probability for the F-test, R^2 is coefficient of determination, and RMSE is the root of the mean square error from the regression model.

were used to describe general seasonal trends in the observed precipitation and throughfall ^{18}O composition (Fig. 2). The sine-wave regression parameters for precipitation and throughfall $\delta^{18}O$ are given by the periodic regression results in Table 1. The seasonal $\delta^{18}O$ amplitudes for Leading Ridge throughfall and Mahantango precipitation were 1.52 and 1.84‰, respectively. Precipitation or throughfall amplitudes given in previous studies in the region were 3.41 and 3.15‰ (DeWalle et al., 1997), and 2.66‰ (Deines et al., 1990). The variation of $\delta^{18}O$ fluctuations at each site was only crudely explained by the sine-wave regressions ($R^2 = 0.241$ and 0.312 for Leading Ridge and Mahantango, respectively); thus, sine-wave methods (Maloszewski et al., 1983) of approximating MRT were not used. However, it is important to show the seasonality (e.g. with sine-wave regression) associated with the input and output $\delta^{18}O$ data, because the signatures are indicators for residence time and provide information regarding weather patterns. The sine-wave regressions between sites were not significantly different ($\alpha = 0.05$) from each other, indicating that seasonal weather patterns are relatively similar at each site.

4.2. Isotopic characterization of output water

The $\delta^{18}O$ signatures of sampled output water (soil water, shallow well water, and streamflow) are shown in Fig. 3. Soil water $\delta^{18}O$ variations at each site show a more rapid response to precipitation or throughfall compared to streamflow and shallow well water $\delta^{18}O$ variations. Soil water samples were unattainable from approximately July 1998 to January 1999 due to drought conditions.

The soil water $\delta^{18}O$ was generally higher during the winter/spring 1999 period than during winter/spring 1998. The first seven tension lysimeter samples at both sites were more depleted in ^{18}O compared to the subsequent samples, with similar trends observed for zero-tension lysimeter soil water. This is likely indicative of inputs with depleted $\delta^{18}O$ prior to the study period and suggests that soil water sampled during these times was a mixture of stored water and incoming new water. Differences in $\delta^{18}O$ patterns between lysimeter types at each site for the entire collection period indicate a different water response time collected by the two different instruments. On an average, the difference in $\delta^{18}O$ between lysimeter types indicates that the zero-tension lysimeters were more enriched in ^{18}O compared to the tension lysimeters and were more similar to precipitation $\delta^{18}O$ composition. At the Mahantango site, the mean difference between zero-tension minus tension $\delta^{18}O$ composition was 0.60‰ and

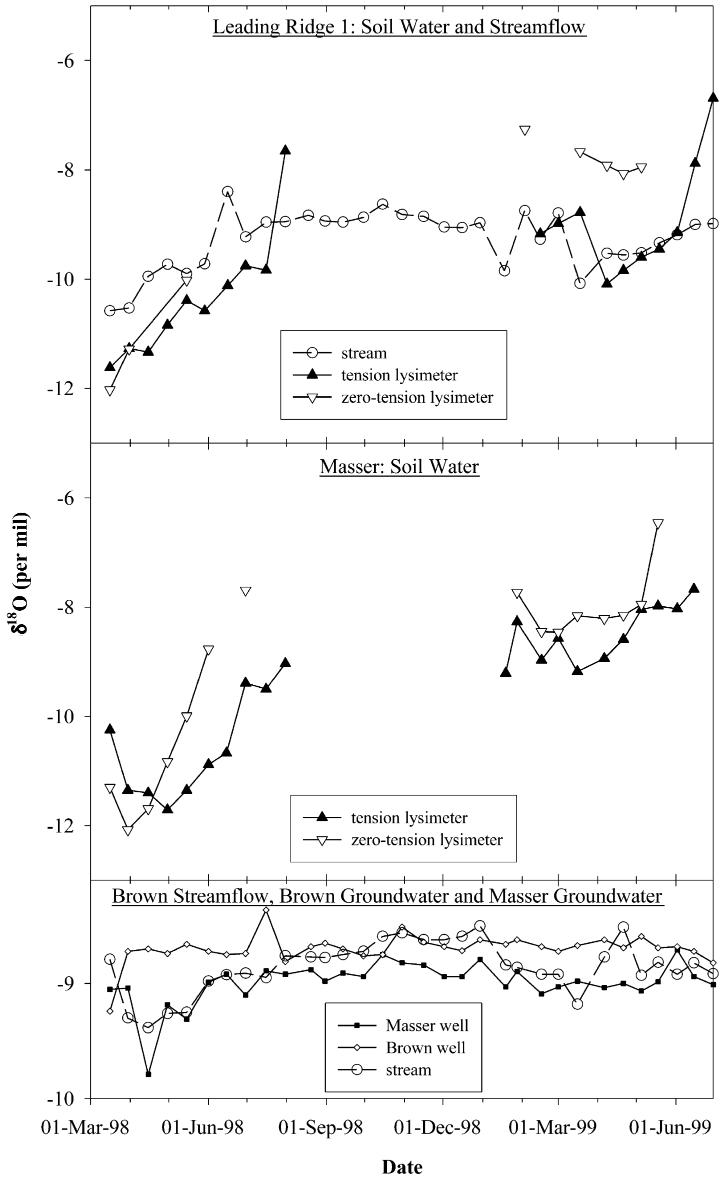

Fig. 3. Output water $\delta^{18}O$ signatures for Leading Ridge and Mahantango sites. Unconnected points were not preceded or followed by another sample.

at Leading Ridge, the difference was 0.95‰, which are both significantly different from zero at $\alpha = 0.05$.

Seasonal variation in $\delta^{18}O$ in streamflow was more pronounced for the Leading Ridge stream (amplitude = 0.52‰) than for Brown stream (amplitude = 0.21‰) (Table 1). Mean annual $\delta^{18}O$ in the streams (−9.20‰ for Leading Ridge and −8.81‰ for Brown) was also significantly different (two-sample t-test, $p = 0.0002$).

The $\delta^{18}O$ seasonal variations in the well water at the Brown (W-AE23) and Masser (W-Cen) sites and the Brown streamflow exhibited small amplitudes (note: W-AE23 sine-wave model is not significant) and were essentially constant for the study period (Fig. 3). The amplitude for the center well at Masser

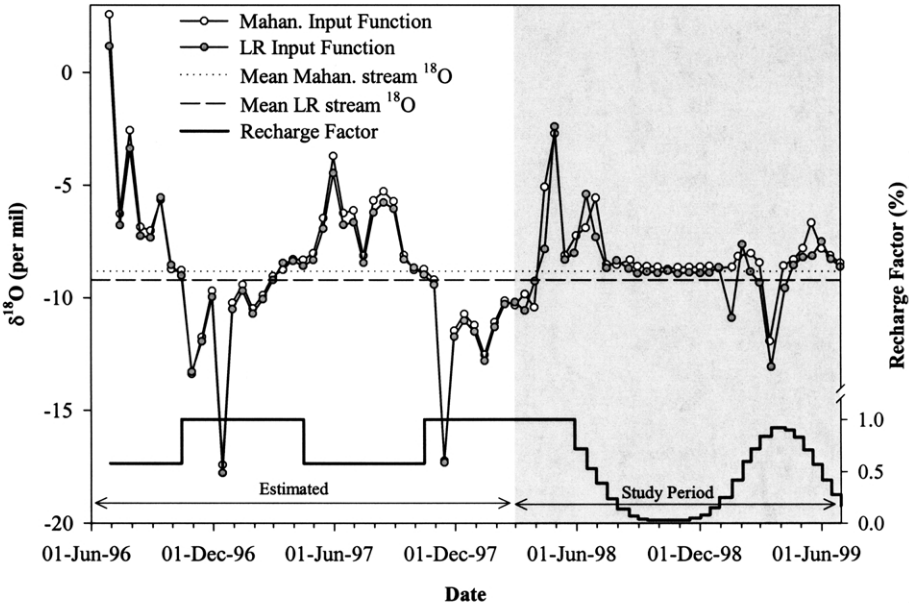

Fig. 4. Calculated δ^{18}O input functions for throughfall at Leading Ridge and precipitation at Mahantango. The dotted and dashed lines represent the mean ^{18}O composition for the Mahantango and Leading Ridge stream, respectively. The shaded region distinguishes the study period from the time when the input function was estimated. Recharge factors are shown for Leading Ridge, which follow a winter/summer weighting during the estimated period and vary seasonally with soil water outflow during the study.

was only 0.03‰ greater than the minimum analytical reproducibility of δ^{18}O determinations. However, median δ^{18}O composition in the two wells and Brown stream were all significantly different from each other at $\alpha = 0.05$ (Kruskal–Wallis test due to non-normal data and Tukey–Kramer multiple comparisons).

4.3. Input functions

Recharge factors were used to adjust the input water amount to represent water that contributed to watershed recharge following a summer/winter α (0.58 and 0.79 for Leading Ridge and Mahantango, respectively) for the estimated past input series, and a sinusoidal α keyed to the time of active soil water movement as observed in the zero-tension lysimeters for the input series during the study period (Fig. 4). The parameters in Eq. (7) determined by manually matching the sinusoid with times of observed soil water movement were: $a_1 = 0.9$, $a_2 = 4$, $a_3 = 0.03$, $\phi = 310$, $\omega = \pi/340$. Fig. 4 shows the calculated input functions that were determined using Eq. (6) (δ_{GW} = mean summer low flow δ^{18}O for each site), which contains the recharge factors that adjust the precipitation and throughfall amounts to represent the varying fraction of input water that contributes to watershed turnover.

4.4. Soil water mean residence time and model results

Soil water MRT estimations were only carried out on spring 1999 samples. As indicated earlier, data from spring 1998 likely reflected stored soil water from a time period prior to this study. The stored soil water may have been mixed with new water during the spring of 1998 yielding water more depleted in ^{18}O than precipitation, thus making MRT estimation during that time inaccessible due to its dependence on the estimated past input data.

MRTs estimated by optimizing Σ (Eq. (8)) for tension lysimeters during the spring 1999 period were 1.6 and 2.2 months for Leading Ridge and Mahantango, respectively (Table 2). The DM was the best-fit model for tension lysimeter soil water at both sites. The D/vx parameters for Leading Ridge (0.10) and Mahantango (0.73) indicate a more piston-flow-like response in tension lysimeter water

Table 2
Solutions for MRTs of soil water (tension lysimeters), stream flow, and shallow well water using best-fit models

Output type/site	Model[a]	Model parameters		Goodness of fit measures					
		Model parameters (η or D/vx)	MRT (months)	Fitting statistic (Σ)	Index of agreement (d_1)	Coefficient of efficiency (E)	Pearson's correlation		RMSE (‰)
							r	p-Value	
Mahantango sites									
Masser tension lysimeters	DM	0.73	2.2	0.1080	0.636	0.501	0.71	0.014	0.36
Brown streamflow	EPM	1.28	9.5	0.0305	0.591	0.411	0.72	< 0.000	0.17
	DM	0.22	7.7	0.0630	0.462	− 1.520	0.69	< 0.000	0.36
Masser well (W-AE23)	EPM	1.08	8.5	0.0359	0.301	− 1.512	0.30	0.094	0.20
Brown well (W-Cen)	EPM	1.23	8.6	0.0369	0.501	− 0.262	0.64	< 0.000	0.21
Leading Ridge									
Leading Ridge tension lysimeters	DM	0.10	1.6	0.1652	0.708	0.701	0.86	0.001	0.52
Leading Ridge 1 stream flow	EPM	1.10	4.8	0.0478	0.725	0.737	0.86	< 0.000	0.27
	DM	0.31	5.2	0.0878	0.602	0.115	0.76	< 0.000	0.50

[a] DM, dispersion model; EPM, exponential-piston model.

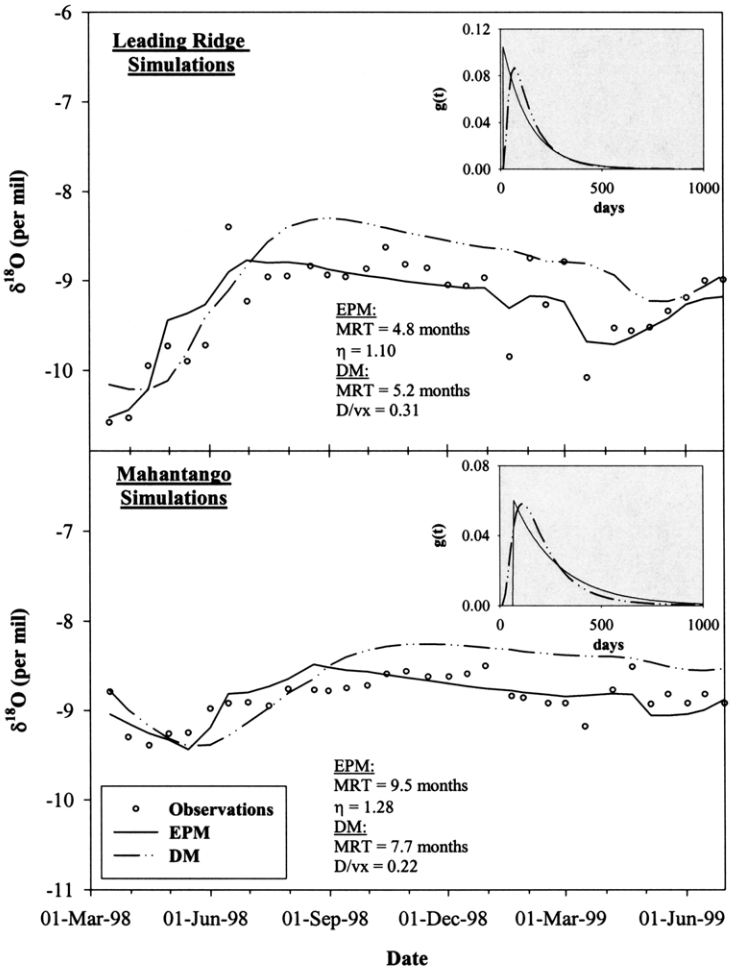

Fig. 5. Model simulations of stream flow. The inset figures show the residence time distributions for the models at each site.

at Leading Ridge. Kreft and Zuber (1978) showed that as dispersion approaches zero (i.e. $D/vx \rightarrow 0$), the system approaches piston flow conditions. Zero-tension lysimeter MRT estimates resulted in unrealistic D/vx parameters for Mahantango, and could not be computed due to a small sample size at Leading Ridge.

4.5. Streamflow mean residence time and model results

Many simulations were performed for streamflow data to assess the MRT and the best-fit models. Model simulations without the extended 20-month input function generally showed higher predicted $\delta^{18}O$ compared to the observed stream $\delta^{18}O$ for input functions that were determined only for the 15-month study period. This suggested that older water with more depleted $\delta^{18}O$ contributed to the measured streamflow and further justified extending the input function prior to the study period. Low $\delta^{18}O$ soil water data that were observed in the first several samples (Fig. 3), also indicated the need for adjusting the input function to account for subsurface flow memory from precipitation prior to the study period with lower $\delta^{18}O$ content. Several simulations using a two-component convolution model (Stichler et al., 1986) were also attempted. These models assumed that only a portion of the input was convolved with the system response function and the remaining

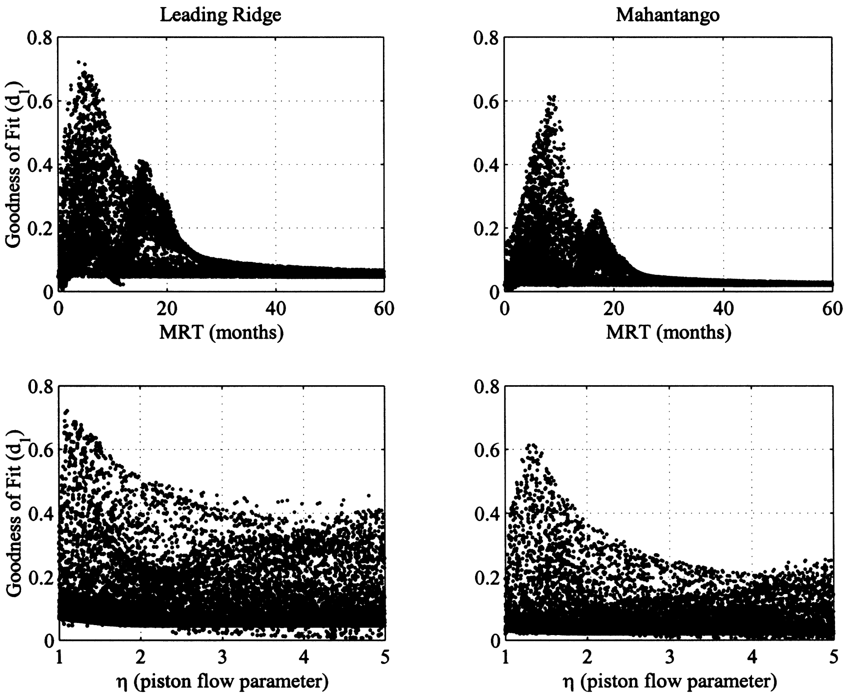

Fig. 6. 20,000 model simulations for streamflow $\delta^{18}O$ using the EPM. Each point represents the goodness-of-fit (index of agreement, d_1) for one model run using randomly selected parameter values.

portion was supplied by a time-invariant older water component (e.g. deep groundwater contribution). Reasonable residence time distributions were achieved; however, there was no geologic evidence to support a second deeper reservoir or establish its true contribution to streamflow.

The exponential-piston flow model (EPM) was the best fitting model for both streams for a given MRT and η. The Leading Ridge stream had a MRT = 4.8 months and $\eta = 1.10$, while Mahantango MRT was 9.5 months and $\eta = 1.28$ (Fig. 5). Higher values of η indicate more PF effect in the flow system. Best fitting DMs were also simulated for each site and are shown in Fig. 5 along with the EPM models. The DM for the Leading Ridge stream had essentially the same MRT as the EPM; however, the MRT for the Mahantango DM (7.7 months) was different from that with the EPM by 1.8 months. The goodness-of-fit statistics in Table 2 shows that the exponential-piston flow models better fit observed data than the DMs did (e.g. $E = -1.52$ and 0.115 for the Mahantango stream and Leading Ridge, respectively). Fig. 5 also shows the residence time distribution functions [$g(t)$] for each best-fit model, which appear to be very similar. However, the time-to-peak residence times for Leading Ridge are 13 and 70 days and for the Mahantango watershed, they are 63 and 126 days for the EPM and DM, respectively.

A Monte Carlo simulation of the models was also used in addition to the non-linear optimization. Fig. 6 shows the computed objective function (i.e. index of agreement) for 20,000 EPM simulations with different combinations of the two model parameters. These plots show the sensitivity of the fit to MRT and piston flow proportion, which indicate that both parameters are well identified and that unambiguous model results can be attained for these data.

4.6. Well water mean residence time and model results

Estimated MRT for Brown well (W-AE23) and Masser well (W-Cen) water were 8.5 and 8.6 months, respectively. However, the coefficient of efficiency

(E) showed that the models fit the observation data poorly ($E < 0$ both wells) (Table 2). The models cannot be used to establish a reliable MRT estimate due to small $\delta^{18}O$ temporal variations and lack of seasonal trend in the well water. A runs test for trends (Minitab, 1998; Gibbons, 1986) in $\delta^{18}O$ for data from the two wells and the Mahantango stream showed that only the stream had a significant trend ($p = 0.0048$), while the Brown well (W-AE23) ($p = 0.9023$) and Masser well (W-Cen) ($p = 0.3330$) exhibited a pattern typical of old water that is difficult to model with $\delta^{18}O$ and appeared to have a random seasonal pattern that may be best described by their respective means.

5. Discussion

5.1. Drought effects

Strong seasonal $\delta^{18}O$ patterns in precipitation and throughfall were not evident in the current study as has been described by other authors (DeWalle et al., 1997; Burns and McDonnell, 1998; Deines et al., 1990; Soulsby et al., 2000). Low R^2 values for the sine-wave regressions suggest only weak seasonality in the data (Mahantango = 0.312 and Leading Ridge = 0.241) (Table 1). Typically, precipitation seasonal $\delta^{18}O$ variations are attenuated in shallow groundwater where the weighted mean annual $\delta^{18}O$ in precipitation is approximately equal to the mean shallow groundwater $\delta^{18}O$ composition (Clark and Fritz, 1997). However, during this study period, drought severely affected recharge to groundwater, which was evident in the difference in mean annual $\delta^{18}O$ input and output waters. The weighted mean annual $\delta^{18}O$ for precipitation (Mahantango = −7.45‰) or throughfall (Leading Ridge = −7.80‰) was significantly greater than that for streamflow (Mahantango = −8.81‰ and Leading Ridge = −9.20‰) and shallow well water (Masser well = −8.97‰ and Brown well = −8.69‰) (Fig. 2). During drought conditions or times of high soil water demand (i.e. from evapotranspiration), larger portions of older water dominate shallow groundwater $\delta^{18}O$ composition and the current year's precipitation $\delta^{18}O$ signature becomes more subdued in subsurface flow.

5.2. Soil water

Soil water MRT investigated in several studies was found to range from about 0.4 to 4 months for various soil types and soil depths ranging from 20 to 80 cm (DeWalle et al., 1997; Lindstrom and Rodhe, 1992; Stewart and McDonnell, 1991). In the current study, MRT estimates using the DM for tension lysimeters at 100 cm depth were 1.6 and 2.2 months for Leading Ridge (LR) and Mahantango (MS), respectively. Vitvar and Balderer (1997) fit a similar DM to lysimeter outflow (220 cm deep) in a hilly pre-alpine basin in Switzerland, and found a MRT of 6.1 months. A greater MRT would be expected at this depth. The resulting best-fit model in the current study for tension lysimeters was the DM with $D/vx = 0.73$ (Mahantango) and 0.10 (LR). The DM used by Stewart and McDonnell (1991) had D/vx values that ranged from 0.14 to 3, while Vitvar and Balderer (1997) had a D/vx parameter of 0.06, which was estimated from a bromide tracer experiment. The tension lysimeter MRT results in the current study agree reasonably well with estimates in previous studies.

Smaller values of D/vx for LR (0.10) suggest that tension lysimeter water responds partially in a piston-like flow manner at this site compared to Mahantango. Stewart and McDonnell (1991) discussed piston-like flow conditions for small values of D/vx as indicating a dominance of advection-flow processes. The smaller D/vx values at Leading Ridge compared to Mahantango suggest that piston flow or advection processes in the soil were a more dominant mechanism at the Leading Ridge site.

Comparisons between $\delta^{18}O$ signatures for lysimeter types suggested that the two devices responded differently, with zero-tension lysimeters more closely tracking precipitation. Wenner et al. (1991) also showed that zero-tension lysimeters responded differently than did tension lysimeters. They found that percolating water sampled by zero-tension lysimeters was intermediate between rainfall isotopic composition and the less mobile water sampled by tension lysimeters. Typically, soil matrix water has longer residence times than water in more mobile pathways, for instance flow in macropores. Since tension lysimeters collect mostly matrix water, the expected MRT would be greater. The difference between zero-tension and tension lysimeters have implications for the selection of lysimeter types used in determining dominant flow mechanisms, response time to stream channel delivery, and in distinguishing 'new' water from stored soil water in streamflow mixing model studies (DeWalle et al., 1988).

MRT for soil water could be used to estimate mobile water content in the unsaturated zone. Such information may be useful for model validation and approximation of depth and time averaged soil water content. The mobile soil water content at Leading Ridge was 4.3% for the 100 cm profile, which was estimated based on a simple reservoir calculation from an assumed recharge rate (i.e. equal to the measured annual stream outflow, $q = 325$ mm/yr) and soil water MRT (1.6 months). At Mahantango, the mobile soil water content was slightly larger (5.2% for the 100 cm profile). The mobile water fraction considered in this estimate contains a mixture of matrix and macropore water, since the MRT estimates were from tension lysimeters.

5.3. Streamflow

The exponential-piston flow model (EPM) was the best-fit model to streamflow. The model describes the condition where the new water fraction initially has no effect on the output water source; thus, the time distribution function is lagged by an amount proportional to $[1 - 1/\eta]$ (Vitvar and Balderer, 1997). For the Mahantango stream, $\eta = 1.28$, which implies that 22% of the total flow volume was piston-flow and did not contribute young water to the system. The Leading Ridge stream had about 9% of the total flow represented as piston-flow. The time distribution functions shown in Fig. 5 show the early portion of the EPM function where new water has no contribution. Piston-flow parameters (η) found in other studies ranged from 1 to 1.2 (Vitvar and Balderer, 1997; Uhlenbrook, 1999).

Interestingly, the best-fit dispersion (DM) and exponential piston-flow (EPM) models at each site had very similar time distributions or response functions (Fig. 5, insets). However, the EPM model fits observed data better than the DM did (Table 2). The peak residence time for the two models reflects the influence of rapid-flow pathways through the watershed such as preferred macropore flow (Unnikrishna et al., 1995). The quick-flow response at Mahantango is much more delayed than Leading Ridge (by approximately 56 days) exhibiting a more regional groundwater response. The DMs at each site have greater time-to-peak residence times than the EPM models, which indicates that the timing of quick-flow contributions in the two model types were different.

Dispersion parameters (D/vx) found in this study (0.10–0.73) were intermediate to optimized D/vx values found in previous studies. Maloszewski et al. (1983) and Herrmann et al. (1999) both found $D/vx =$ 0.15 for obtaining best-fit streamflow simulations. However, Maloszewski et al. (1992) and Vitvar and Balderer (1997) found much higher values of $D/vx =$ 0.6 and 0.7, respectively, for obtaining best-fit streamflow models. Higher D/vx values indicate a more heterogeneous hydrologic system with relatively high variation in flow path length throughout the watershed.

In all simulations, MRT is less for Leading Ridge (LR) compared to the Mahantango stream (MS), which is counterintuitive because the LR basin is approximately nine times larger than the MS basin. Vitvar and Balderer (1997) estimated MRT using both DM and EPM models and found MRT = 12.5 months for a 318 ha pre-alpine watershed. DeWalle et al. (1997) used the simple sine-wave method and found MRT = 18 months for two small Appalachian watersheds (approximately 40 ha). Greater seasonal variation observed at LR may be due to shallow flow paths controlled by soil fragipans typical of all the soil series at LR, which range in depth from 0.5 m on the upper slopes to 2.0 m on the lower slopes (Lynch and Corbett, 1989). This emphasizes the importance of subsurface topographic features in streamflow generation.

MRT at the Leading Ridge stream was 4.8 months, which corresponds to a mobile water storage volume of approximately 130 mm (i.e. $V_m = \text{MRT} \times q$, where q is the annual runoff, 325 mm/yr). The mobile water storage volume at the Mahantango site ($q = 285$ mm/yr) was 225 mm. These approximate volumes could be used to compare contributing volumes during non-storm conditions so long as average effective porosities were known; however, these data were not available for our study sites.

5.4. Shallow well water

Model simulations for the wells were not able to fit observed data ($E < 0$), but the sine-wave regression models for the Masser well (W-Cen) showed that the residence time was longer than that for the Mahantango stream. This was evident in the lower amplitude (0.14‰) for W-Cen compared to 0.21‰ for the Mahantango stream, and the greater time to maximum response (about 18 days more). The best-fit models that were obtained for the well data had less piston-flow effect (based on η than the Mahantango stream (MS), indicating a more complete distribution of flow path lengths. Landon et al. (2000) found that maximum transit time through a shallow (2.8–4.5 m) sandy unsaturated zone varied from 2 to12 months, thus, the much deeper shale system (approximately 8–15 m) in the current study would have longer expected residence time.

Since both wells were located on topographic mounds or watershed divides, it can be assumed that the well locations represent the point of maximum vertical flow in the watersheds. It is intriguing that this vertical flow pathway through the unsaturated zone had an ^{18}O signature with greater damping than streamflow. This suggests that on average, the residence time of flow paths contributing to streamflow were less than water percolation through the unsaturated zone in the watershed divide position and that streamflow is a relatively shallow flow system.

6. Conclusions

Residence time distributions were used to describe the difference between average flow conditions that existed in two watersheds. Dispersion and exponential piston-flow models were found to be the best response function models to describe subsurface flow conditions and estimate mean residence time for soil water and stream baseflow in two mid-Appalachian small watersheds. Both models can have similar residence time distributions; however, the exponential piston-flow model, which lacks young water contribution, provided the best simulation for streamflow ^{18}O and the dispersion model was better for estimating soil water ^{18}O. mean residence times found for streamflow were less than one year (4.8–9.5 months) and soil water mean residence times were about 2 months, representing approximately 5% mobile soil water content. Even though the residence time models considered did not fit shallow well water, it was shown that the flow pathways comprising stream water were shorter than recharge to the groundwater table. The inclusion of input function adjustments (e.g. the addition of past input data and varying recharge factors during the drought period) can improve the accuracy in residence time determination, especially during drought conditions. This study demonstrates that during times of high soil water demand, ^{18}O in meteoric water becomes subdued and older subsurface water begins to dominate streamflow ^{18}O signatures.

Acknowledgements

Financial support during this study was provided by the School of Forest Resources, the Environmental Resources Research Institute and the US Geological Survey through the State Water Institute Program (project no. 1434-HQ-96-GR-02694). In addition, sample analysis assistance was provided by USDA-ARS. Assistance with equipment maintenance and sample collection at the Mahantango sites was provided by the USDA-ARS Klingerstown staff. The authors also wish to thank Bryan Swistock, Karl Williard, Anthony Buda, Michael Gockley, Adam Kaeser, Todd Strohecker, and Michael Demchik for assisting with fieldwork. We would like to express our appreciation to Piotr Maloszewski for his helpful discussions, suggestions, and review. We also thank Peter Cook, Brian Swistock, and Jeff McDonnell for critical reviews and valuable comments.

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