



Seasonal ^{18}O variations and groundwater recharge for three landscape types in central Pennsylvania, USA

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Received 13 November 2003; revised 9 August 2004; accepted 17 August 2004

Abstract

Seasonal ^{18}O variations in precipitation, soil water, snowmelt, spring flow and stream baseflow were analyzed to characterize seasonal dynamics of groundwater recharge in three central Pennsylvania catchments. The catchments represented three common landscape types: Valley and Ridge-shale (Mahantango Creek), Valley and Ridge-carbonate (Buffalo Run), and Appalachian Plateau-sandstone (Benner Run). Samples were collected on a biweekly basis from May 18, 1999 to May 9, 2000. Precipitation, soil water, and baseflow isotopic composition data indicated that a seasonal recharge bias existed for these catchments, most recharge occurred in the fall, winter, and spring months. An altitude effect of -0.16 to $-0.32\text{‰}/100$ m change in elevation was discernible in precipitation, soil water, and stream baseflow isotopic compositions. Soils effectively damped seasonal variations of recharge ^{18}O composition after depths of 1.62–2.85 m. The greatest damping of the annual isotopic composition signal occurred in the shallow soil layers (0–15 cm). In these and similar landscapes with thick soils the annual isotopic composition signal may be completely damped prior to reaching the stream as baseflow. Isotopic variations measured in stream baseflow are more likely to be caused by the shallow flowpath water relatively close to the streams. Baseflow stable isotope variations found on the basins studied suggested that residence times for subsurface waters to reach channels were much longer than the annual seasonal cycle of ^{18}O in precipitation. Damping depths were similar for the three different catchments but it is not certain how spatially variable damping depths were within each catchment. This information would be useful in determining areas within catchments that contribute to short term isotopic composition fluctuations within streams ('new water'). Predictive models that determine isotopic damping depth from meteorological, soil and vegetation/land-use data can help develop a better understanding of the variability of recharge and attenuation of contaminants across the landscape.

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Keywords: Stable isotopes; Attenuation; Elevation; Appalachians; Natural recharge; Oxygen 18

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1. Introduction

Seasonal stable isotope variations in precipitation have been used to study the movement and the source of subsurface water in various settings (Kendall and McDonnell, 1998). The stable isotopes of H (D) and O (^{18}O) occur naturally in precipitation and provide a seasonal meteoric signal in temperate, continental systems that is often attenuated in shallow groundwater (Clark and Fritz, 1997; Frederickson and Criss, 1999; Abbott et al., 2000). The input signal becomes more pronounced in snow-dominated systems where snowfall and snowmelt can be depleted in heavy isotopes of H and O relative to rainfall (Maule et al., 1994). The attenuation of precipitation signals by the underlying catchment has been used to evaluate the mean residence time for stream baseflow using sinusoidal relationships and other models that describe flow path distributions (Maloszewski et al., 1983; Pearce et al., 1986; DeWalle et al., 1997; Burns et al., 1998; Soulsby et al., 2000). These models assume that the isotopic attenuation reflects the mean residence time of transport from recharge through the entire flow system and that the recharge is uniformly distributed in time.

Recharge isotopic composition may be modified from the snowmelt and rainfall signal by evaporation or by mixing and diffusional exchange with stored water held in the soil pores within the unsaturated zone. In humid regions, evaporation effects are usually small and processes involving hydrodynamic dispersion and exchange with less mobile pore space are the primary influences on the alteration of the isotopic signature of precipitation (Barnes and Turner, 1998). The percolation of precipitation through heterogeneous, variably saturated soils results in a smoothing of the seasonal isotopic composition with depth. The loss of seasonal variation with depth is known as the 'critical depth' and is defined as the depth at which annual variations in the isotopic composition do not exceed the analytical precision of $\delta^{18}\text{O}$ determinations (Clark and Fritz, 1997).

During the period of May 18, 1999–May 9, 2000, we measured the seasonal ^{18}O variations in stream baseflow, spring flow, soil water, precipitation and snowmelt with reference to three common landscape types in central Pennsylvania (Valley and Ridge-shale, Valley and Ridge-carbonate,

Appalachian Plateau-sandstone). The objective of this study was to use ^{18}O variations in natural waters to improve the understanding of the seasonal dynamics of recharge, evapotranspiration, and contributing area to streams in central Pennsylvania. Field quantification of water movement through catchments is an important step towards characterizing a variety of large-scale surface water quality problems, such as acidic deposition and agricultural non-point source pollution.

1.1. Early isotope hydrological studies conducted in central Pennsylvania

A variety of stable isotope hydrological studies have been conducted in central Pennsylvania (Deines et al., 1990; Pionke and DeWalle, 1992, 1994; DeWalle and Pionke, 1994; DeWalle and Swistock, 1994; DeWalle et al., 1997; McGuire et al., 2002). A summary of several isotope hydrological studies in central Pennsylvania concluded that the mean annual ^{18}O composition of precipitation within the Spring Creek watershed of central Pennsylvania is enriched in ^{18}O compared to mean annual groundwater composition, and therefore it is likely that summer precipitation does not contribute significantly to recharge in this region (Deines et al., 1990). At a location with permeable soils on the mountain slopes in the Nittany Valley, Deines et al. found that the isotopic composition of soil water can have significant seasonal variability at depths of up to 9 m (annual isotopic damping depth).

DeWalle et al. (1997) found an average annual isotopic damping depth (the depth at which annual isotopic composition variations drop to below $1/e$) of 49 cm for two forested basins in West Virginia (Fernow Experimental Forest) and one in central Pennsylvania (Benner Run), using simple, periodic regressions for seasonal variations. They calculated mean residence times of 0.2 years for precipitation to percolate to a depth of 30 cm in soil, 1.1–1.3 years for precipitation to be discharged as spring flow and 1.4–1.6 years for precipitation to be discharged as stream baseflow on the smaller catchments in West Virginia. The larger catchment (Benner Run, PA) showed no detectable seasonal fluctuations in baseflow ^{18}O composition, indicating that flow emanated from sources with mean residence times greater than about 5 years.

In a recent study, McGuire et al. (2002) evaluated mean residence time for stream baseflow and soil water in the Brown Catchment (Mahantango Creek Experimental Watershed, Klingerstown, PA) and another central Pennsylvania site (Leading Ridge Experimental Watershed, Huntingdon County, PA). The authors found that mean residence times for soil water at 100 cm depth was 2 months for both sites and for stream baseflow, 9.5 months and 4.8 months, respectively.

2. Site descriptions

The three study sites are located in central Pennsylvania. Mahantango and Buffalo Run sites are located in the Valley and Ridge Physiographic Province and the Benner Run site is located on the Appalachian Plateau (Fig. 1a). Central Pennsylvania has a humid northeastern continental type climate. Mean annual precipitation is approximately 1090 mm at Mahantango Creek (Gburek and Folmar, 1999), 970 mm at Buffalo Run (Parizek and White, 1985), and 1000 mm at Benner Run (DeWalle et al., 1993).

The Benner Run site (Fig. 1b) is located in the northern portion of the Appalachian Plateau Province of Pennsylvania. The catchment encompasses an area of 11.34 km², with a maximum elevation of 740 m and minimum elevation of 650 m (DeWalle et al., 1993). The land-cover is forest, which is dominated by deciduous mixed oak (*Quercus* spp.), maple (*Acer* spp.) and black cherry (*Prunus serotina* L.). The Pocono Group (Burgoon and Shenango sandstones) underlies the Benner Run catchment. The soil distribution consists of well-drained Hazleton and DeKalb soils (Typic Dystrochrepts) and Andover and Laidig series soils (Typic Fragiaquults and Typic Fragiudults) containing greater clay content and shallow fragipans. Depth to bedrock is typically greater than 5 m. The soil pit was excavated in the Hazleton series, a sandy loam. A more detailed description of the site is provided in (Johnson, 1996; DeWalle et al., 1993).

The Mahantango Creek (Fig. 1c) site is managed by the USDA-ARS (Gburek, 1977) and consists of the WE-38 watershed, a sub-watershed of East Mahantango Creek, a tributary of the Susquehanna River. The catchment drains an area of 7.3 km², with 45%

of the land area forested and the remaining 55% predominantly agricultural cropland. Within the catchment elevations range from 225 to 480 m above sea level. The catchment is underlain by the Trimmers Rock and Catskill Formation, which consist of sandstone (uplands), siltstone (inter-bedded with sandstone and shale, mid-portion of the catchment) and shale (lower portion of the catchment). The residual soils are typically shallow (<1.5 m) and consist of Hartleton (Typic Hapludult) and Berks (Typic Dystrochrept) channery silt loams (Pionke et al., 1996). The soil pit is within the Calvin series, a shaley silt loam. A full description of the site is provided by Gburek and Folmar (1999).

Buffalo Run (Fig. 1d) lies within the Nittany Valley of central Pennsylvania, the first northeastern valley of the Ridge and Valley Physiographic Province of Pennsylvania. The upper 24.5 km² portion of this catchment was included in this study. In this upper portion of the catchment, elevation ranges from 555 m on Bald Eagle Ridge to 332 m at Waddle, PA, our lowest monitoring location (BUF 5). The catchment is underlain by folded and faulted carbonate rocks (predominantly the Bellefonte formation) in the valley and shales and sandstones (predominantly Juniata and Reedsville Formations) on the Bald Eagle Ridge. The stream joins Spring Creek at Bellefonte, Pennsylvania. Parizek and White (1985) provide a detailed description of the geologic setting of the entire Spring Creek watershed.

Residual soils in some portions of the catchment may be as thick as 50 m (O'Driscoll and Parizek, 2003). The most extensive soil association within the catchment is the Hagerstown (Typic Hapludalf)—Opequon (Lithic Hapludalf)—Hublersburg (Typic Hapludalf) association formed from limestone and dolomite bedrock, which exists along the carbonate valley (Ciolkosz and Dobos, 1992). The Buffalo Run soil pit was located 5.3 km to the east of the stream sampling location BUF5 (at the Pennsylvania State University Radioastronomy wastewater irrigation site). The pit was excavated in Hagerstown silt loam soils, which often have a clay layer in the subsoil (Braker, 1981). Land-use consists of forest on the shale/sandstone uplands (48%) and predominantly agriculture (34%, both pasture and cropland) and housing developments (8%) in the carbonate valley (Sengle, 2002).

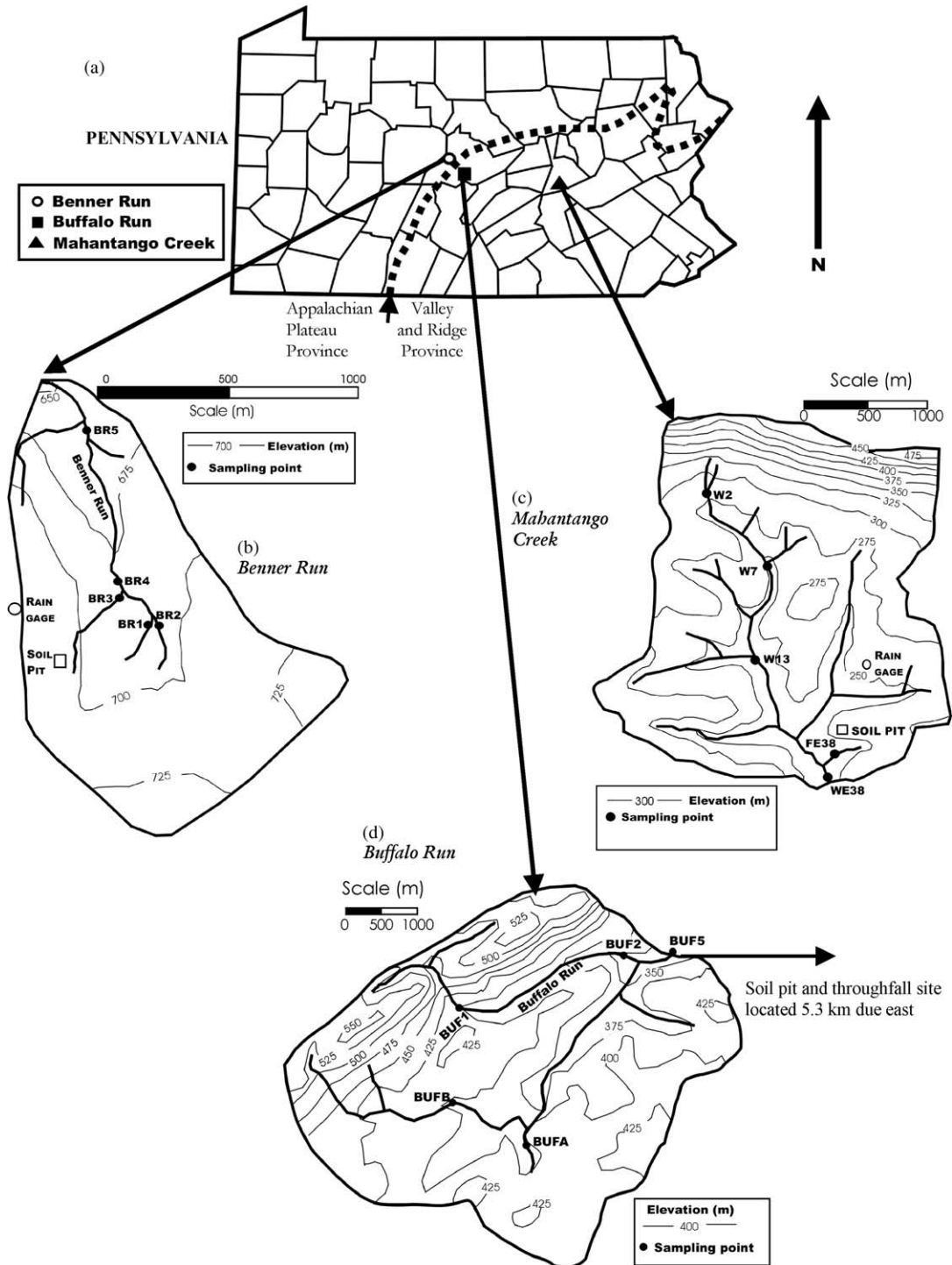


Fig. 1. Locations of the three study catchments (a) and topography and sampling locations for Benner Run (b), Mahantango Creek (c), and Buffalo Run (d).

Precipitation amounts during this study (May 1999–2000) were 100 mm above average for Mahantango Creek (1190 mm), 220 mm below average for Benner Run (780 mm), and 70 mm below average for Buffalo Run (900 mm). Mild to extreme drought conditions were present in central Pennsylvania beginning in September 1998 and continuing for the duration of the study. Previous studies have estimated evapotranspiration at 60% of precipitation for Mahantango Creek watershed (Gburek, 1977; Gburek and Folmar, 1999), 65–70% for the Spring Creek watershed containing Buffalo Run (Giddings, 1974) and from a simple water budget, undertaken by us using streamflow and biweekly precipitation data, 65% for Benner Run.

3. Methods

3.1. Data collection

Water samples of precipitation, snowmelt, soil water, stream baseflow, and spring flow were collected at each site. The sampling occurred over the period of May 1999–2000. Precipitation, soil water, streamflow and springflow samples were collected at biweekly intervals and snowmelt was collected during melt events in snowmelt lysimeters. Soil water was collected at depths of 15, 30 and 90 cm below grade. One soil water monitoring pit was excavated for each site, containing both pan (zero-tension) and tension lysimeters (60 kPa of tension was applied and water was extracted on biweekly visits). Pan lysimeters were 320 cm² polyethylene trays back-filled with the excavated soil and horizontally placed in the sidewall of the excavation. Ceramic porous cup tension lysimeters were used in conjunction with pan lysimeters. At each site there were two pan and two tension lysimeters for each depth, for a total of 12 lysimeters per site. Samples from each depth were composited by lysimeter type for each sampling date that soil water was collected.

Surface water was monitored at five locations within each watershed, four of these locations consisted of streamflow and one location for spring discharge. Spring flow was collected at one spring at Mahantango (W2), one spring in the Buffalo Run catchment (BUFA), and one spring at Benner Run

catchment (BR3). Stream and spring sampling was conducted generally during baseflow conditions. Streamflow monitoring stations were located at nested elevations at each study site. At Benner Run surface water sampling sites, elevations ranged from 686 to 652 m and catchment areas varied from 1.1 ha to 8.9 km², respectively. At Buffalo Run surface water sampling sites, elevations ranged from 400 to 335 m and catchment areas varied from 1.7 to 24.5 km², respectively. At Mahantango Creek surface water sampling sites, elevations ranged from 230 to 279 m above sea level and catchment areas varied from 0.14 ha to 7.3 km², respectively. Baseflow sampling locations are shown for all sites in Fig. 1b–d.

Precipitation was collected as throughfall (Benner Run, Buffalo Run) or open precipitation (Mahantango) at the excavated soil pits for each site. Screened funnels (530 cm²) at an elevation of 1 m above grade collected precipitation/throughfall at two locations per pit. The funnels were connected by tubing to a sample reservoir buried in the soil pit, to ensure that the water sampled remained cool in order to minimize evaporation between sampling periods. A loop was created in the tubing to prevent water vapor from migrating out of the sample reservoir. For each sampling date a composite sample was collected with equal amounts of water from the two site samplers.

Snowmelt was collected at each site at the ground surface in a polyethylene tray (2788 cm²) that drained to a snowmelt-sampling reservoir in the soil pit. Snowmelt water was typically removed from the reservoir within several days of the melt event. From hereafter we will refer to precipitation, throughfall and snowmelt as precipitation.

3.2. Oxygen-18 analysis

For the study, 813 water samples were collected and analyzed for ¹⁸O composition by mass spectrometry (Epstein and Mayeda, 1953) at the Stable Isotope Laboratory, Southern Methodist University, Dallas, Texas. The ¹⁸O composition was reported in per mil units relative to Vienna Standard Mean Ocean Water (VSMOW). The analytical precision of $\delta^{18}\text{O}$ results was 0.09‰ (1 standard deviation) based on 35 blind duplicate pairs.

4. Results and discussion

4.1. Seasonal recharge

The mean annual isotopic compositions of precipitation, soil water and baseflow varied among the three catchments (Fig. 2). At all sites a similar trend existed, mean annual precipitation composition was enriched in ^{18}O relative to mean annual baseflow and deep soil water (90 cm depth) isotopic composition. This indicates that recharge at these locations was seasonally biased and more likely to occur during the cooler periods of the year, when typical ^{18}O compositions of precipitation in this region are relatively depleted.

The differences between weighted mean annual precipitation and mean baseflow ^{18}O composition at specific sites were -1.96‰ (BNR), -1.53‰ (BUF), and -1.37‰ (MAH) (Fig. 2). These differences are related to the amount of precipitation that is not recharged. The deficit may be larger if soil water evaporation occurred. However, Deines et al. (1990) found that fractionation due to soil water evaporative losses in the Nittany Valley (Buffalo Run) were minimal, based on a comparison of the local meteoric water line and groundwater ^{18}O vs. D relationships. Transpiration is likely the predominant component of evapotranspiration in these watersheds and transpiration losses do not result in isotopic fractionation in the remaining soil water (e.g. Wershaw et al., 1966; Dawson and Ehleringer, 1991).

The variation in precipitation, soil water and baseflow isotopic composition throughout the year is

expressed as the coefficient of variation (standard deviation/mean $\times 100\%$) (Fig. 2). Mean annual baseflow coefficient of variation ranged from 0.42 to 3.55% for the stream locations where samples were collected. Much of the variation in the annual precipitation isotopic signal (CV = 47.7–56.9%) was attenuated when measured at depths of 90 cm in the soils (CV = 8.1–12.3%). The isotopic composition seasonality that was evident in precipitation and soil water was further subdued in baseflow (Fig. 2).

Annual isotopic composition coefficient of variation consistently decreased with depth and generally isotopic composition of mean annual soil water became more depleted in ^{18}O relative to mean annual precipitation. However, this relationship did not always hold for the shallow soil water (15 and 30 cm). Benner Run (15 and 30 cm) and Buffalo Run (15 cm) soil water samples had mean annual isotopic compositions that were enriched in ^{18}O relative to precipitation. At Benner Run the enrichment difference was 0.63‰ at 15 cm and 1‰ at 30 cm and at Buffalo Run the enrichment difference was 0.56‰ at 15 cm. This indicates that evaporation at the surface (prior to infiltration) and in the shallow soils resulted in more enriched isotopic composition values. The difficulties in sampling soil waters at Buffalo Run at all depths for each sampling date may have affected these results.

Seasonal recharge was observed at all sites, represented by soil water presence in 90 cm tension lysimeters. Soil water was collected in the (90 cm) tension lysimeters predominantly during fall and spring months (Fig. 3). Buffalo Run (90 cm) tension

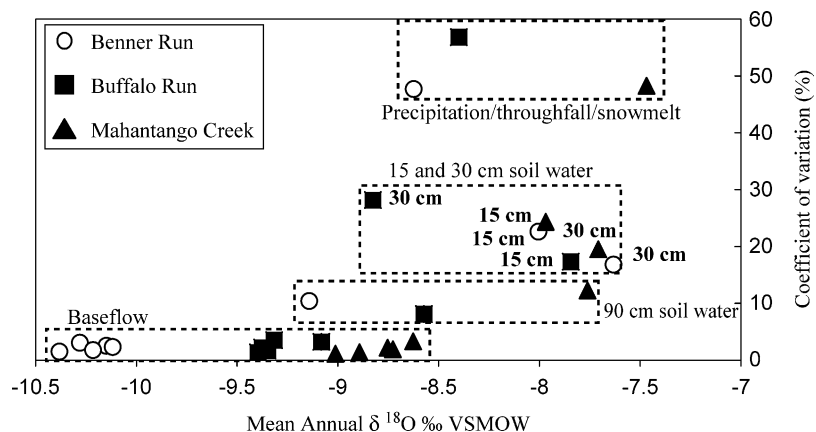


Fig. 2. Summary of mean annual $\delta^{18}\text{O}$ ‰ and coefficient of variation (%) for mean baseflow, mean soil water at 15, 30 and 90 cm (suction and pan lysimeters), mean precipitation and snowmelt (Mahantango Creek), and mean throughfall and snowmelt (Benner Run and Buffalo Run).

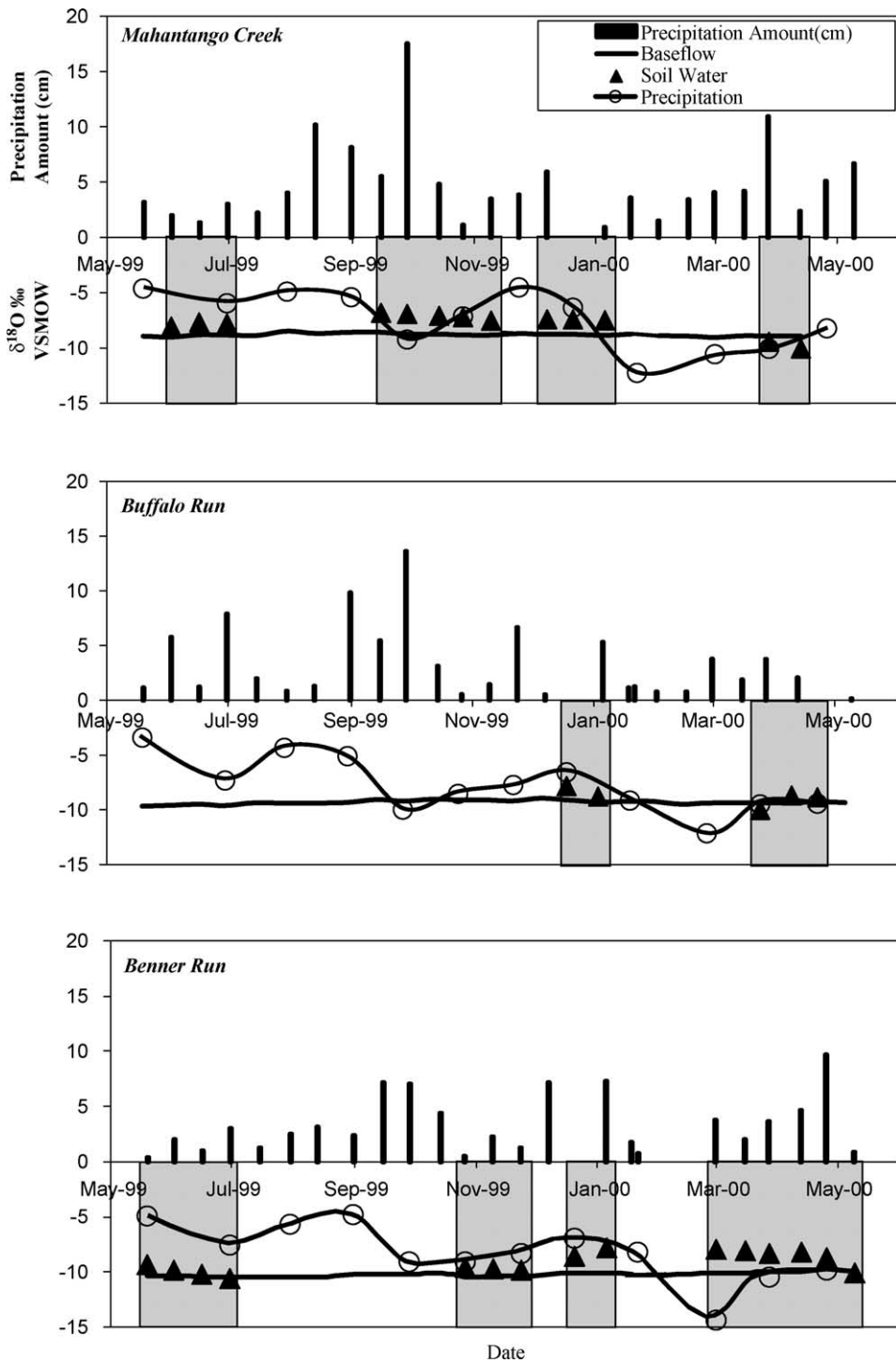


Fig. 3. Mean weighted precipitation and snowmelt, 90 cm (tension lysimeter) soil water, mean baseflow and precipitation amounts for May 18, 1999–May 9, 2000. Gray areas indicate periods of soil water collection in 90 cm tension lysimeters (recharge).

lysimeter data reveal that deep percolation is less likely at this site; soil water was only collected for two general periods during the winter of 1999 and spring of 2000. At the Buffalo Run soil water sampling site, subsoil clay was present and sample collection was more difficult throughout the year. Therefore, the results obtained at the Buffalo Run soil pit were probably not representative of the entire catchment. Overall, these soil water data indicated that fall and spring months were the most important for recharge at these sites but winter recharge may also have occurred. This seasonal recharge bias allowed for the estimation of annual evapotranspiration at the sites.

4.2. Evapotranspiration estimates

Monthly weighted mean isotopic composition of precipitation ($\delta^{18}\text{OP}$) at each site was calculated as the monthly mean $\delta^{18}\text{O}$ times the monthly precipitation amount divided by the yearly precipitation amount. The exclusion of growing season (May–September) data for the calculation of $\delta^{18}\text{OP}$ caused the difference between precipitation isotopic composition and mean annual baseflow isotopic composition to decrease substantially. Similar results were found by Deines et al. (1990), Abbott et al. (2000), and McGuire et al. (2002). The changes in this study were -1.96 to -0.64‰ (BNR), -1.53 to -0.28‰ (BUF) and -1.36 to -0.36‰ (MAH), indicating that this seasonal precipitation was not likely contributing to the baseflow signature. Removing the related monthly precipitation amounts from the site-specific totals provided a means to estimate the minimum amount of

precipitation that did not recharge the groundwater (i.e. due to evapotranspiration) for the year. The annual ratio of evapotranspiration to rainfall was estimated by dividing the growing season precipitation amount by the total annual precipitation amount.

Evapotranspiration estimates from isotope data were reasonably close to those calculated from water budgets for the sites (37–60% of annual precipitation, Table 1). However, the Benner Run estimate was substantially different, which may have been a result of the below average growing season precipitation total for this year of study. This estimation may vary if significant changes in storage occur during the year (i.e. long residence times) and thus, it represents a long-term average estimate because the annual precipitation input signal may not be translated to the stream within the same year.

Similar calculations were performed using the 90 cm soil water data. The analyses indicated that the removal of June and July isotopic composition precipitation data resulted in values similar to the soil water isotopic composition. After removal of the associated precipitation amounts, estimates of transpiration losses in the upper 90 cm of soils ranged from 10.6 to 21.6% of total annual precipitation (Table 1).

4.3. Altitude effect

A consistent landscape-scale pattern of ^{18}O enrichment existed in isotopic composition of precipitation, 90 cm soil water and baseflow proceeding west to east from Benner Run to Buffalo Run to

Table 1

Differences between weighted mean annual precipitation and baseflow ^{18}O composition for all field data and for non-growing season data

Baseflow	Benner Run		Buffalo Run		Mahantango Creek	
	($\delta^{18}\text{O}\text{‰}$)	(%)	($\delta^{18}\text{O}\text{‰}$)	(%)	($\delta^{18}\text{O}\text{‰}$)	(%)
Difference						
All field data	-1.96	19.17	-1.53		16.48	15.54
Non-growing season data	-0.64	6.26	-0.28		3.07	4.05
ET estimate from isotope data		37.4			59.8	48.0
ET from water budgets		65			65	60
References				Giddings (1974)		Gburek (1977)
90 cm Soil water						
All field data	-0.87	9.55	-0.53		6.33	4.32
Excluding June and July	-0.54	5.93	-0.14		1.64	-0.86
Losses in the top 90 cm of soil		19.2			21.6	10.6

Evapotranspiration estimates based on non-growing season ^{18}O composition are included.

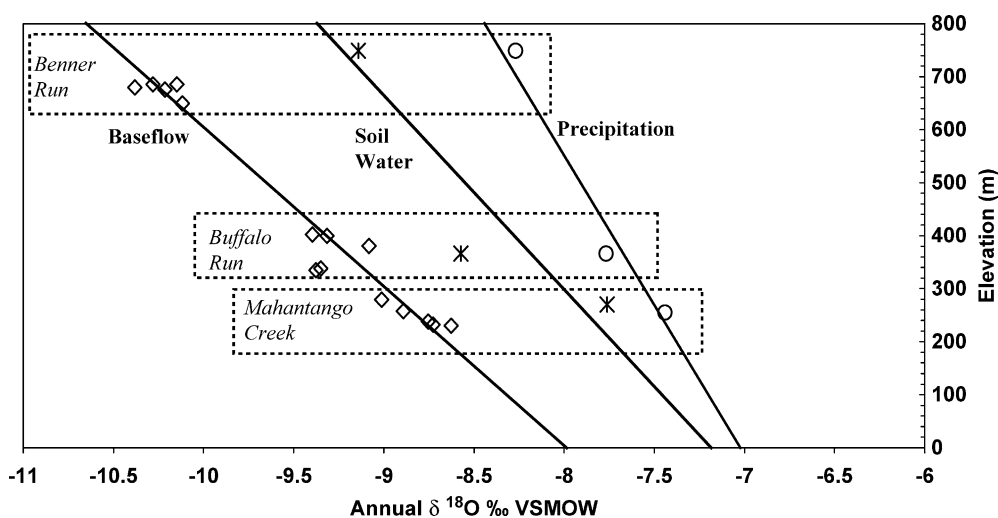


Fig. 4. Altitude effect expressed as mean annual ^{18}O composition of baseflow, 90 cm soil water and precipitation (Mahantango Creek)/throughfall (Benner Run, Buffalo Run) and snowmelt. Slope of baseflow regression line = $-0.32\text{‰}/100\text{ m}$, 90 cm soil water = $-0.30\text{‰}/100\text{ m}$, and precipitation = $0.16\text{‰}/100\text{ m}$. Average altitude effect = $-0.26\text{‰}/100\text{ m}$.

Mahantango Creek (Fig. 2). This pattern was attributed to sampling location elevation differences. A mean altitude effect of $-0.26\text{‰}/100\text{ m}$ change in elevation was calculated based on mean precipitation, mean soil water (90 cm), and mean baseflow isotopic composition for all sites (Fig. 4, Table 2). Both baseflow ($-0.32\text{‰}/100\text{ m}$) and 90-cm soil water ($-0.30\text{‰}/100\text{ m}$) estimates produced similar slopes.

An altitude effect estimated from mean annual precipitation data alone was $-0.16\text{‰}/100\text{ m}$ change in elevation. This effect varied seasonally depending on the trajectory of weather systems and the source/temperature of cloud vapor masses. The altitude effect estimates fell within a range of published values of -0.15 to $-0.5\text{‰}/100\text{ m}$ change in elevation (Clark and Fritz, 1997).

The seasonal variation of altitude effect was evaluated by comparing monthly isotopic composition values vs. elevation for precipitation, soil water, and baseflow (Fig. 5). The soil water and baseflow

elevation effects were more depleted in ^{18}O because of a seasonal recharge bias. Baseflow data showed the most consistent pattern with a steady drop in elevation effect from August 1999 ($-0.39\text{‰}/100\text{ m}$) to May 2000 ($-0.20\text{‰}/100\text{ m}$). This was likely a translated effect resulting from precipitation isotopic composition differences between sites that occurred prior to the study. Soil water and precipitation data showed much more variability with respect to seasonal elevation effect. Soil water behaved consistently with baseflow. The soil water and baseflow altitude effects always remained negative, that is, as altitude increased isotopic composition became more depleted in ^{18}O . The soil water pattern was unclear due to the lack of samples during dry periods.

The precipitation data contained several points throughout the year that had positive elevation effects (Fig. 5). Although the majority of data points fell in the negative elevation effect range, three points were positive, August and October 1999, and February

Table 2

Altitude effects calculated from isotopic compositions ($\delta^{18}\text{O}$) of precipitation, soil water and baseflow at various elevations in central Pennsylvania

Altitude effect $\delta^{18}\text{O}\text{‰}/100\text{ m rise } (R^2)$	Precipitation	Soil water (90 cm)	Baseflow	Published values (Clark and Fritz, 1997)
	-0.16 (0.97)	-0.30 (0.83)	-0.32 (0.91)	-0.15 to -0.5
Average effect	-0.26			

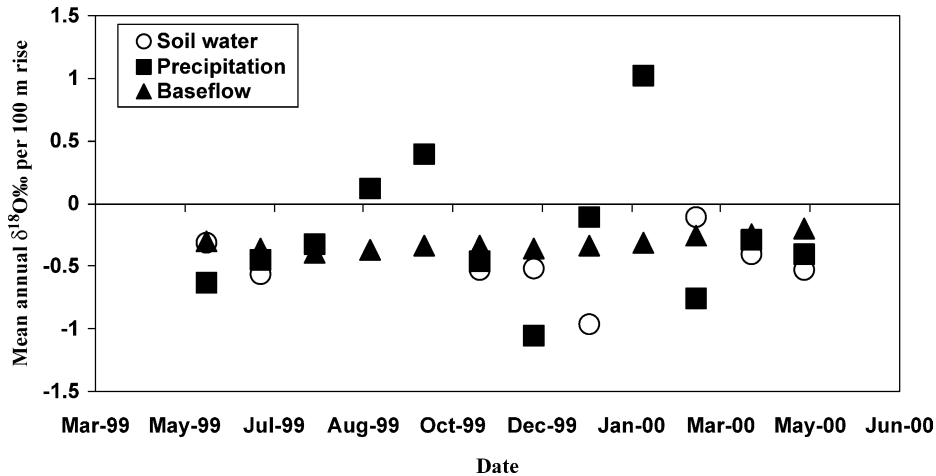


Fig. 5. Seasonal variation of altitude effect calculated from mean monthly soil water, precipitation, and baseflow isotopic composition for all sites. Elevation effect is presented as change ‰ per 100 m change in elevation.

2000. These data indicated that precipitation elevation effect varied seasonally due to the effect of cloud vapor mass source and weather type. During typical recharge periods, the elevation effect was negative and this effect was translated to soil water and baseflow.

4.4. Precipitation and snowmelt variation

A general pattern of depletion in precipitation ^{18}O occurred for all sites from the beginning of the study in May 1999 (average precipitation $\delta^{18}\text{O} = -4.3\text{‰}$) throughout the study, with mean precipitation $\delta^{18}\text{O}$ measured at approximately -9‰ at all sites at the end of the study (Fig. 6). Weighted mean monthly precipitation isotopic compositions were similar for the three locations with some variability for several of the sampling periods. For the study year, mean weighted precipitation isotopic composition was -8.54‰ at Benner Run, -7.95‰ at Buffalo Run, and -7.43‰ at Mahantango Creek. The range of annual variation for precipitation and snowmelt at the sites was -19.00‰ (Benner Run), -19.61‰ (Buffalo Run), and -13.13‰ (Mahantango Creek). The smaller range at Mahantango Creek was a result of less snowmelt relative to the other sites.

Snowmelt isotopic composition showed more variability among sites. During January and February 2000, snowmelt measured at all locations was generally depleted in ^{18}O relative to precipitation

and this input resulted in a more negative spike in the data, with a range of snowmelt $\delta^{18}\text{O}$ of -8.97 to -22.92‰ . The sample most depleted was collected from a January melt event at Benner Run. These data revealed that significant snowmelt events could result in pulses of isotopically depleted recharge waters. The isotopic composition of the meltwater is related to the fractionation processes in the snowpack (Taylor et al., 2002).

4.5. Soil water

In some cases, the snowmelt composition spike was observed in lysimeter water shortly after a melt event. For example, this occurred on February 1, 2000 (MAH and BUF) and February 29, 2000 (BNR) (Fig. 6). The spike at 30 cm at Buffalo Run without a corresponding spike at 15 cm indicated that preferential flow occurred that bypassed the soils around the shallower lysimeter. Recharge was possible in the winter months.

Soil water data collected in tension lysimeters were similar to those collected in pan lysimeters. Pan lysimeter data was slightly more variable, as evident in the coefficient of variation of annual isotopic composition of 22.4% compared to that of tension lysimeters of 14%. Mean differences between isotopic composition of all paired tension and pan lysimeter soil water data for each specific site and depth were not statistically significant at $\alpha = 0.05$ ($n = 41$), thus

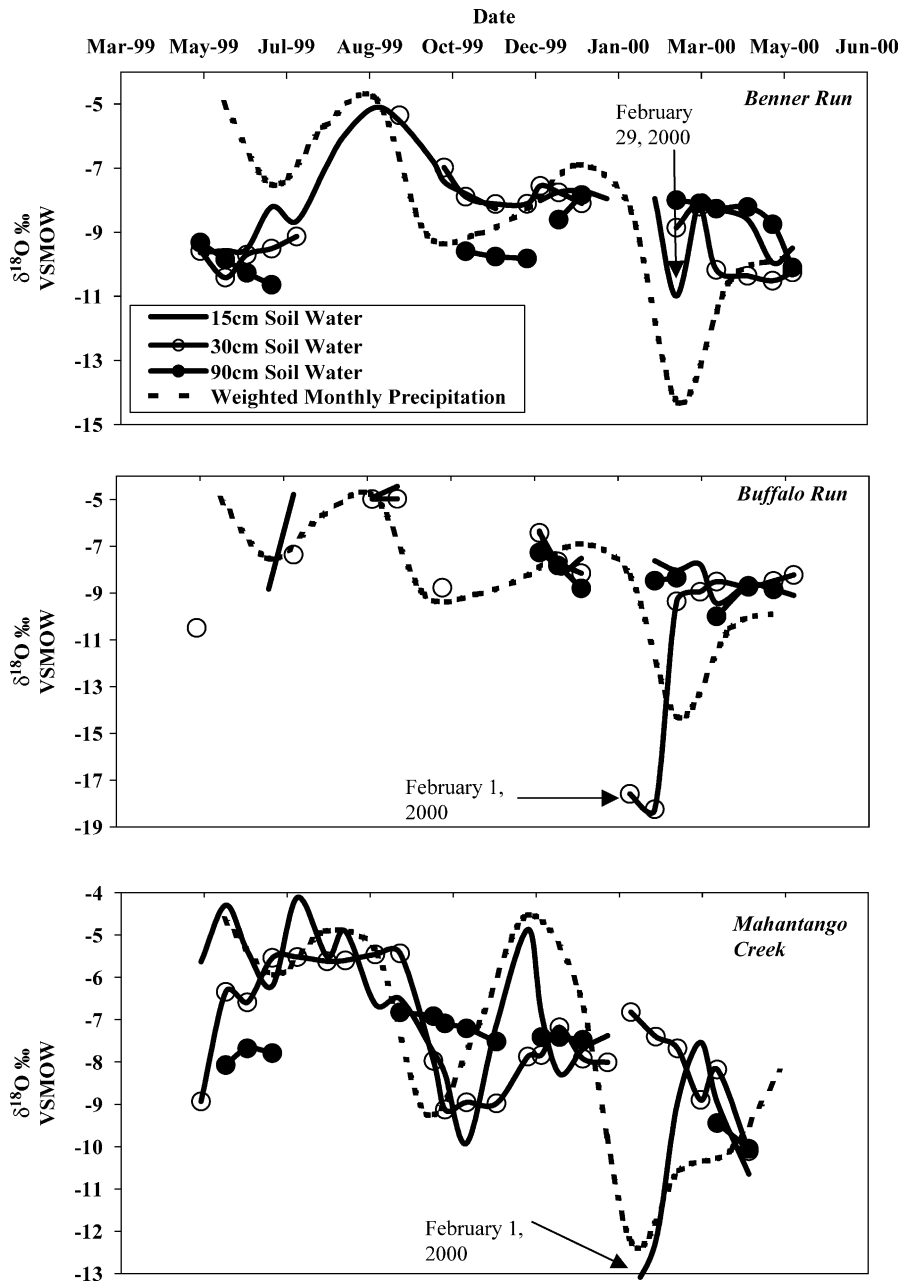


Fig. 6. Mean soil water ^{18}O composition for 15, 30 and 90 cm soil water collected in pan and suction lysimeters and monthly mean weighted isotopic composition of precipitation and snowmelt at Benner Run, Buffalo Run, and Mahantango Creek for the period of May 18, 1999 to May 9, 2000.

soil water values used in this paper are averages of both tension and pan lysimeters if both samples were collected during that period. DeWalle et al. (1988) also showed no statistically significant differences

between soil water collected by tension and pan lysimeters in a forested Appalachian catchment in central Pennsylvania. However, several studies have argued that soil water composition sampled from

these devices can be different even when collected at similar depths and from similar soils (e.g. Wenner et al., 1991; Leaney et al., 1993; McGuire et al., 2002).

Soil water ^{18}O composition varied with depth and location (Figs. 2 and 6) but direct comparison between specific sites, depths, and device (i.e. pan vs. tension lysimeter) was complicated by variability in sample collection. In some cases, only one site sample was collected from either the tension or pan lysimeter for a specific depth and date. During the summer months, soil water composition was typically depleted in ^{18}O relative to the precipitation input and in many cases no samples were collected by lysimeters, indicating that recharge was not occurring during the summer months of 1999.

Mean annual soil water ^{18}O at 90 cm depth was enriched in ^{18}O relative to baseflow for all sites. This indicates that soil water either mixed with soil water or groundwater that was more depleted in ^{18}O prior to discharge, or that due to the drought conditions during this study, the deeper soil water represents a pulse of water that was generally more enriched in ^{18}O than the long term average discharge. Based on peaks in soil water isotopic composition depleted in ^{18}O relative to peaks in precipitation isotopic composition, it was estimated that soil water mean residence times range from 2 weeks in the shallow soils (15 cm) to approximately 8 weeks in the deeper soils (90 cm) (Fig. 6). However, more detailed modeling of the isotopic data is needed for more accurate soil water residence time estimates (e.g. McGuire et al., 2002).

4.6. Isotopic damping depth

The annual isotopic composition coefficient of variation generally decreased with soil depth. The 30 cm soil water at Buffalo Run had a greater coefficient of variation than the 15 cm soil water. This discrepancy is likely due to the presence of shallow clay at the site. A logarithmic relationship with soil depth existed between the coefficient of variation of precipitation and soil water annual isotopic composition. This relationship was used to calculate the soil depth at which the input signal would become damped to levels similar to mean baseflow at each site (mean annual baseflow isotopic composition coefficient of variation at Buffalo

Run = 2.43%, Benner Run = 2.25% and Mahantango Creek = 1.74%) (Fig. 7). To provide baseflow with coefficient of variations similar to those measured for baseflow at the various stream locations would require precipitation to infiltrate, travel, and disperse through less than 3 m of soil. The Buffalo Run site contained soils that could damp the signal sufficiently by 1.62 m. Similarly, Benner Run contained soils that could damp the signal by 1.90 m and Mahantango Creek had the greatest damping depth of 2.85 m. The Buffalo Run site contains soils with greater clay content than those at Mahantango Creek or Benner Run. This indicates that the presence of clay soils can reduce damping depth. These calculated depths could vary annually depending on the antecedent moisture, timing, amount and isotopic composition of precipitation. Vegetation also likely exerts a strong influence on damping depth, as the soil pits located in forested areas below the canopy (Benner Run and Buffalo Run) exhibited shallowest damping depths and the soil pit located in an open field area (Mahantango Creek) displayed the deepest damping depth.

DeWalle et al. (1997) found an average annual isotopic damping depth of 49 cm using soil depth as the flow path length for three Appalachian forested watersheds (including Benner Run). In that case, the damping depth was defined by a reduction in variation of $1/e$, or 63%. To obtain variations similar to those measured in our streams would require a reduction of approximately $1/e^4$, or 98%. This would require a multiplication factor of four for the DeWalle et al. (1997) damping depth estimate, which would result in a comparable damping depth estimate of 1.96 m. Soil water damping depth determined from data reported by McGuire et al. (2002) for tension lysimeters within the Mahantango site was 2.1 m, which is also in close agreement with values determined in this study.

These damping depths suggest that the annual isotopic composition signal may be completely damped prior to reaching the stream as baseflow. Thus, the residence time through the unsaturated zone is likely greater than the residence time of baseflow. McGuire et al. (2002) found similar results and suggested that on average, flowpaths comprising baseflow were shorter than vertical recharge through the unsaturated zone to the groundwater table. Results from Assano et al. (2002) agree; they found that soil

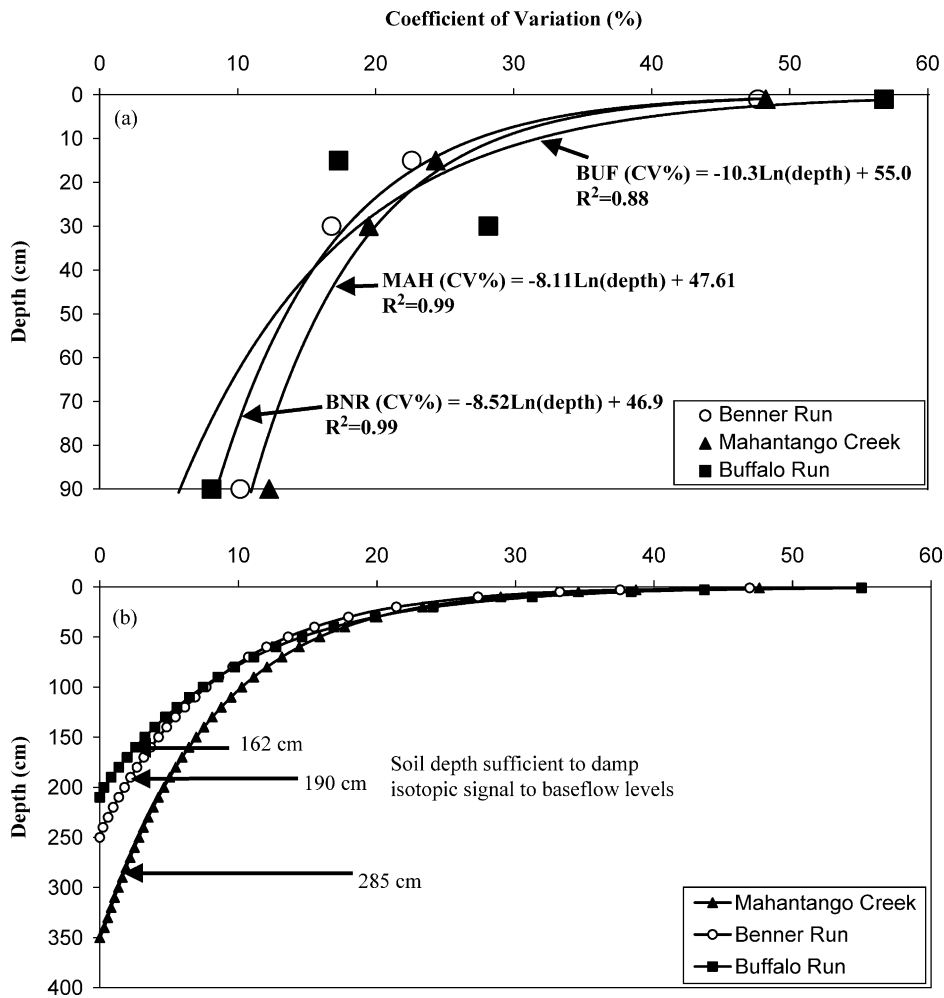


Fig. 7. (a) Logarithmic relationships for each site between annual ^{18}O composition coefficient of variation (%) and soil depth (cm) for the period of May 18, 1999 to May 9, 2000. (b) Isotopic damping depth calculated using site-specific logarithmic equations presented in (a). Soil depths sufficient to damp annual ^{18}O composition coefficient of variation to baseflow variation are 162 cm (Buffalo Run), 190 cm (Benner Run) and 285 cm (Mahantango Creek).

water and transient groundwater mean residence time depend on the length of vertical infiltration.

Kirchner et al. (2000, 2001) found fractal temporal scaling of contaminant concentrations in stream water that suggests the timing of input variations of a contaminant relative to the residence time distribution of subsurface waters on a basin controls the temporal pattern of baseflow response. Short-duration variations of input contaminants relative to the variation in residence times would produce relatively large attenuation, while input contaminant variations with a time scale greater than residence times for

subsurface waters could be transmitted to streams relatively un-attenuated. Dispersion or exponential distribution models also show travel time distributions with long tails (i.e. McGuire et al., 2002). In our study, we are looking at attenuation of the annual ^{18}O pattern in input rainfall with modification due to preference for recharge of winter–spring precipitation. The fact that the annual pattern of ^{18}O in precipitation is highly attenuated in stream baseflow suggests that an annual cycle is relatively short compared to the residence time distribution for subsurface waters on these basins. Thus, precipitation on these Pennsylvania

Table 3
Slope of annual coefficient of variation of isotopic composition of precipitation and soil water at various depths at Benner Run, Mahantango Creek and Buffalo Run soil pits

Slope-CV vs. depth (% CV/cm depth)	Benner Run	Mahantango Creek	Buffalo Run
0–15 cm	–1.67	–1.59	–2.63
15–90 cm	–0.16	–0.16	–0.12
Difference in slope factor (0–15 cm)/(15–90 cm)	10.09	9.90	21.49

basins appears to have taken several to many years to reach a channel as baseflow.

The majority of the damping of the annual isotopic composition signal of precipitation occurs in the upper 15 cm of soil. The slopes of coefficient of variation vs. depth for the upper 15 cm of soil are on average 14 times greater than those for the soil column from 15 to 90 cm deep (Table 3). Thus, most damping of the isotopic signal occurs in a relatively shallow soil layer. This may be explained by interception and water uptake by vegetation, both of these factors contribute to removing water from the shallow soil layer, with the majority of removal occurring during the growing season when canopies are fullest and water uptake is greatest. The removal of growing season precipitation water prior to recharge results in less annual variation in shallow soil water isotopic composition when compared to annual variation in precipitation isotopic composition.

Despite soil damping of seasonal ^{18}O signals found in this study, DeWalle et al. (1997) did find a clear seasonal variation in stream baseflow and springflows on two small, steep, forested catchments at Fernow experimental forest in West Virginia. They used this seasonal signal to estimate mean residence times for baseflow and springflow waters of about 1.1–1.6 years. In contrast, baseflow data from the larger Benner Run, Pennsylvania basin in the DeWalle et al. (1997) study showed little seasonal ^{18}O variations in baseflows. They attributed this difference in seasonal patterns largely to a difference in basin size and secondarily to slope steepness and soil depth in the valley. Estimated mean residence time for baseflow on Benner Run was greater than 5 years. In the current study we deliberately sampled headwater catchments in Pennsylvania with areas similar to those at Fernow and still found no appreciable seasonal variations.

The greater slope steepness on the West Virginia basins may actually explain this difference in seasonal ^{18}O variations in baseflows. Water that moved through the soil on the steeper West Virginia catchments could have been delivered through or over bedrock surfaces quickly enough to preserve the seasonal ^{18}O variations, while recharge water moved slowly enough on the less-steep Pennsylvania basins to completely mix with other waters and damp the seasonal signal.

4.7. Spatial variability

Due to the heterogeneous nature of catchments it is likely that point estimates of isotopic composition of rainfall and soil water will not be representative of the entire catchment. In the catchments studied, spatial variability of the isotopic input signal is a result of the measured altitude effect, variations in precipitation amount, variations in vegetative cover, soil type, and soil depth. For the range of elevations within each catchment the elevation effect would result in a difference in rainfall isotopic composition of 0.23‰ (Benner Run), 0.61‰ (Buffalo Run), and 0.66‰ (Mahantango Creek) between the highest and lowest points within these catchments.

Orographic effects may result in spatial variation in rainfall amounts in central Pennsylvania (Barros and Kuligowski, 1998). Based on a detailed meteorological study by Reich (1966) it was determined that 30 rain gages provided an adequate sampling of rainfall for the entire 378 km² Spring Creek watershed. This spacing is sufficient to overcome spatial variability (including orographic effects) for this watershed. Extrapolating these results indicates that one gage per 12.6 km² would be appropriate for these central Appalachian settings. This gage density was met for Benner Run and Mahantango Creek; however, Buffalo Run had only one gage for a 24.5 km² catchment area. The spatial variability of rainfall amount within these catchments is likely to vary most during convective thunderstorms that typically occur between June and August and are often very localized (Giddings, 1974). However, most of the rainfall during the study period occurred during the fall and spring when frontal storms tend to distribute rainfall more evenly across the landscape.

Spatial variations in vegetative cover and interception of precipitation can result in variations in the isotopic input signal. Throughfall isotopic composition measurements should provide a good estimate of the composition of the isotopic input signal for the Benner Run catchment because it is entirely forested. For the Buffalo Run catchment, throughfall was used and this is likely more representative of the isotopic input signal than open precipitation for this catchment because forest covers approximately one half of the catchment area and the majority of the upland areas within the catchment are entirely forested. For Mahantango Creek, open precipitation was used to represent the isotopic composition input signal because the majority of the catchment area was agricultural land. The differences between weighted open precipitation (Mahantango Creek) and throughfall (Buffalo Run and Benner Run) did not differ significantly based on paired two sample *t*-tests ($\alpha=0.05$). Based on these observations it is likely that point measurements of isotopic input composition collected on a biweekly basis were representative of the actual inputs to these catchments.

Soil pits were sited in locations where soils were thought to be representative of the catchment. However, due to spatial heterogeneity of geology, topography, soil types and vegetation within each catchment it is likely that the soil water isotopic composition variations observed represent only a subset of the actual compositions that exist within each catchment.

A detailed study conducted at the Mahantango Creek site (watershed WE-38) used a water balance modeling approach to quantify the effects of the spatial variability of soil type and vegetation cover on evapotranspiration, runoff, and groundwater recharge (Yu et al., 2000). They found that soils with the highest available water capacity (typically silt loams and clay loams) generally exhibited the highest rates of evapotranspiration and runoff when compared to other sandy loam soils within the catchment. Sandy loam soils typically had higher groundwater recharge rates. Vegetation (crop-type) was found to have a greater influence on spatial variability of runoff and evapotranspiration than soil type. For the 72904 block cells simulated over the entire watershed (7.3 km²), groundwater recharge varied across the Mahantango

Creek (WE-38) catchment from 8 to 35 cm for the 1984–1985 water year.

Based on the Yu et al. study, the degree to which the soil water data measured at pits is representative of the catchment could be ranked from most reliable at Benner Run, where vegetation cover and soil type are most homogeneous, to least reliable at Buffalo Run, where the watershed area is much larger and geology, soil type and land use vary the most.

5. Conclusions

The precipitation, soil water, and baseflow data for all sites indicated that year-round recharge did not occur during the study period in these central Pennsylvania watersheds. Recharge occurred only during brief periods in spring, fall and winter months. The lowest occurrence of recharge was observed at Buffalo Run, possibly due to clay-rich soils. Mean residence time models that use the precipitation isotopic composition signal as input may require a recharge weighting factor, to account for the typical absence of recharge during the growing season in this and other regions.

The isotopic input signal also varied due to elevation. An altitude effect explains some of the differences in mean annual precipitation ¹⁸O composition among the three landscape types. The effect was observed in precipitation, soil water and baseflow at the three sites. This altitude correction of -0.16 to $-0.32\text{‰}/100$ m change in elevation can be significant for isotope hydrology studies in the Appalachians or other mountainous regions, even where elevation differences between ridgetops and valley floors seldom exceed 300 m. The effect varied seasonally, with the maximum gradient observed in precipitation in December 1999 of $-1.06\text{‰}/100$ m change in elevation.

The soil water data collected at 3 discrete locations for the various landscapes indicated that soils at these sites effectively damped the seasonal variation of precipitation isotopic composition at depths of 1.62–2.85 m. The greatest damping of the annual isotopic composition signal occurred in the shallow soil layers (0–15 cm). These data indicate that in settings with thick soils the annual isotopic composition signal may

be completely damped prior to reaching the stream as baseflow. This is significant because after recharge is translated to streams, a large proportion of baseflow may have little or no annual isotopic composition variation. This study demonstrates that in various landscape settings a large component of the isotopic variations that occur annually in baseflow of streams are likely to be caused by the shallow flowpaths relatively close to the streams or by lateral preferential flow of soil water or groundwater.

Damping depths were similar for the three different settings but it is not certain how spatially variable damping depths were within each catchment. This information would be useful in determining the areas within a catchment that contribute to short term isotopic composition fluctuations within streams, the component of streamflow that contributes to these fluctuations is commonly referred to as 'new water'. Delineation of likely source areas for 'new water' could identify areas near streams most likely to contribute contaminants during runoff events. For instance, episodic acidification of streams occurs because 'new water' inputs are not neutralized. A better understanding of likely source areas of 'new water' inputs could help watershed managers to focus liming efforts to mitigate acidic episodes.

One approach would be to construct damping depth maps of catchments to document the potential volume of catchment responsible for rapid drainage. This could be accomplished by using a calibrated modeling approach that accounts for soil type and vegetative cover, similar to the one discussed earlier for quantifying spatial variations in groundwater recharge by Yu et al. (2000). Although installation of soil pits and lysimeters across the landscape could also be used to measure spatial variability of damping depths, this approach may be a logistical challenge. It may be possible to simplify field measurements of damping depth by using a soil gas approach to collect time series of soil water ^{18}O composition data at various depths and locations across the landscape (Tang and Feng, 2001). Predictive models that determine isotopic damping depth from meteorological, soil and vegetation/land-use data can help develop a better understanding of the spatial variability of recharge and attenuation of contaminants across the landscape.

Acknowledgements

Financial support during this study was provided by the School of Forest Resources and the Institutes of the Environment, The Pennsylvania State University, and the US Geological Survey through the State Water Institute Program project number USDI-1434-HQ-96-GR-02694. In addition, equipment maintenance and sample collection assistance was provided by the USDA-ARS Klingerstown staff. The authors thank Anthony Buda, Patricia Craig, Michael Gockley, Dana McGuire, Pete Sharpe, Todd Strohecker, Michael Reiner, and Karl Williard for assisting with fieldwork. We also thank the anonymous reviewers for helpful comments and suggestions that improved this manuscript.

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