Stable isotope tracers in watershed hydrology

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Introduction

Watershed hydrology is a field of study that concerns itself with questions of where water goes when it rains, what flowpaths the water takes to the stream, and how long water resides in the watershed. Even though these questions seem basic and water-focused, they often form the underpinning for questions of water availability, biogeochemical cycling, microbial production, and other ecological processes that depend on the water cycle. While stable isotopes of water (e.g., $^{1}H_{2}{}^{16}O$ and $^{1}H^{2}H^{16}O$) have been used to study global-scale water cycling since the early 1950s (Epstein & Mayeda 1953; Craig 1961; Dansgaard 1964), they were not used for watershed-scale problems of water source, flowpath, and age until the 1970s (Dinçer et al. 1970). Sklash & Farvolden (1979) were among the first hydrologists to quantify the composition of stream water and its temporal and geographical sources using water isotopes in small watersheds. Since then, watershed-scale stable isotope hydrology has blossomed (Kendall & McDonnell 1998), and today, stable isotopes are a standard tool for helping hydrologists understand the basic functioning of watersheds. More importantly, stable isotope tracing and analysis forms an important link between hydrological and ecological processes at the watershed scale where knowledge of flow path, water source, and age inform many water-mediated ecological processes.

This chapter shows how an understanding of watershed hydrology is fundamental to watershed ecology. We also show that rather basic isotope techniques can help to better understand water quality, sustainability, land-use change effects, nutrient cycling, and general terrestrial and aquatic system interactions. We first review basic concepts in watershed and stable isotope hydrology, and then present some isotope-based approaches relevant to the hydrology–ecology interface.

Basic concepts in watershed hydrology

Our introduction to the basic concepts in watershed hydrology is to provide readers with a background for understanding hydrological systems so that

cross-disciplinary linkages are realized. For more advanced material pertinent to isotope hydrology, the reader may wish to consult one of several good books and book chapters written on this topic by Gat & Gonfiantini (1981), Sklash (1990), Coplen (1993), Coplen et al. (2000), Clark & Fritz (1997), Kendall & McDonnell (1998), and Buttle & McDonnell (2004). Here, we restrict ourselves to an overview of stable isotope techniques in small watersheds, which we define as 10^{-2} to 10^{2} km^{2}. Our overview of watershed hydrology is from a process-oriented perspective, i.e., focused on physical and functional relationships to the generation of streamflow (the drainage of water to streams). More detailed treatment of this topic can be found in Anderson & Burt (1990), Bonell (1998), Buttle (1998), Dunne & Leopold (1978), and Ward & Robinson (2000).

The water balance

Watersheds are hydrologic systems where inputs and outputs of water, sediment and nutrients are cycled within topographically restricted landscape units (Dunne & Leopold 1978). As such, the watershed serves as the control volume where mass is conserved according to the following water balance equation:

$$\frac{dS}{dt} = I - O = P - Q - ET \tag{11.1}$$

where dS/dt are changes in water storage within the watershed, I are watershed inputs, equivalent to P (precipitation), and O are the watershed outputs. Variables Q and ET are the streamflow discharge (runoff) and the evapotranspiration, respectively. This equation can be further simplified when looking at long-term averages, since changes in the volume of stored water (dS/dt) are typically small compared with the remaining terms; thus, dS/dt can be neglected. While equation 11.1 illustrates the most simple of conceptual hydrologic frameworks, the dynamic terms on the right-hand side of the equation can be difficult to quantify or understand in detail. This is especially the case for the transfer between terms (i.e., flow pathways), and is where isotope tracers have been most useful.

Streamflow generation processes

Water flow pathways control many ecological processes, biochemical transformations, exchange reactions, and mineral weathering rates. For example, stream nutrient dynamics are often very sensitive lateral flow paths through shallow organic mats or other zones where water may mobilize or flush labile constituents. Flow paths determine largely the geochemical evolution along the flow gradient and the contact time in the subsurface (or residence time) has much control on the translocation of weatherable products in the soil and bedrock.

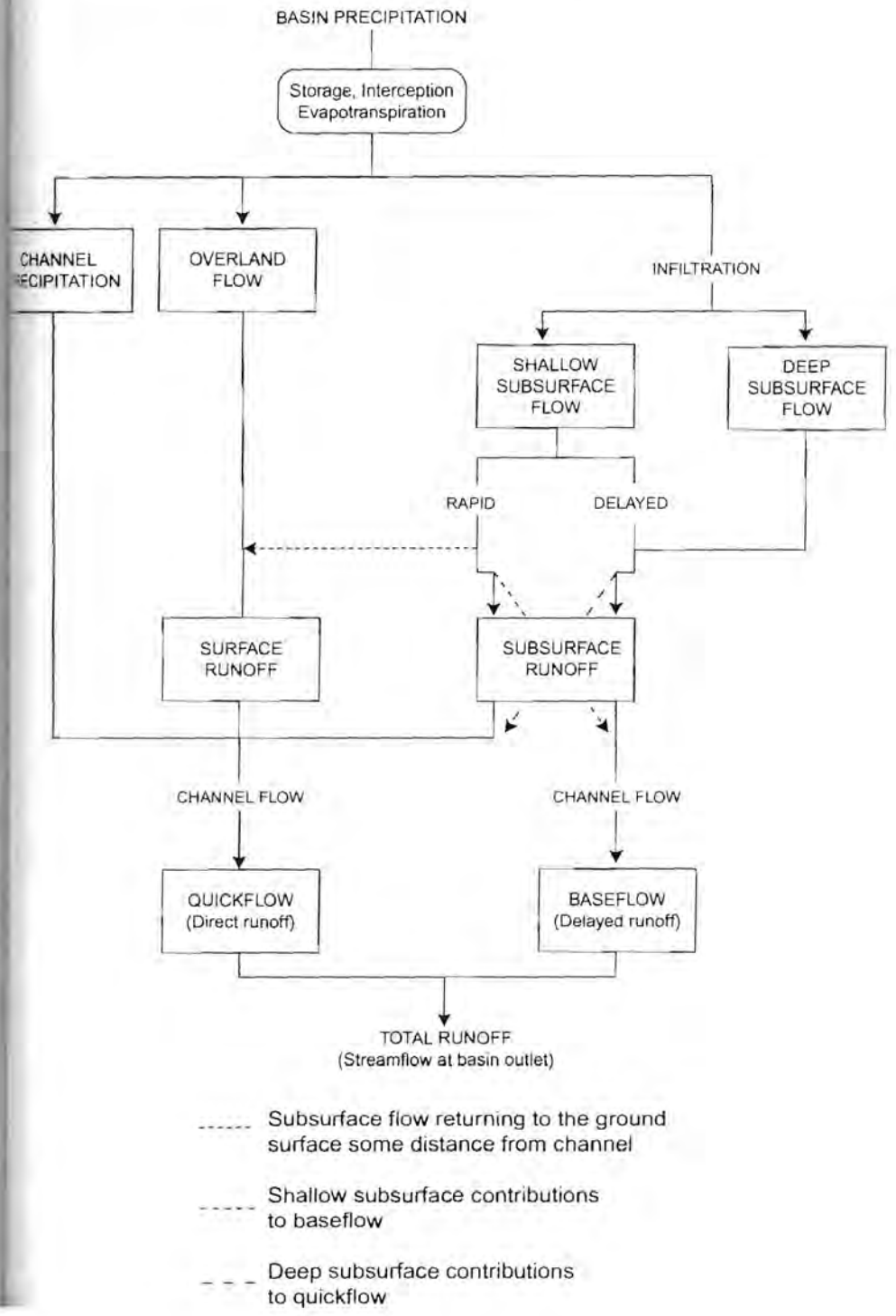
Equation 11.1 shows that precipitation is balanced by the sum of stream discharge and evapotranspiration. Thus, the proportion of precipitation that contributes to streamflow is what remains after considering several losses, including the evaporation of intercepted precipitation by the vegetation canopy and ground cover (e.g., litter), evaporation from the soil, and transpiration. Transpiration (i.e., passive water loss through plant stomata driven by climatic forces) is generally assumed to be minimal during storm events, since vapor pressure deficits are low and leaf surfaces are wet (Penman 1963). During wet canopy conditions, transpiration reduction is partly compensated by the evaporation of intercepted precipitation (Stewart 1977; Klaassen 2001). However, transpiration exerts significant control on antecedent soil moisture conditions by plant extraction of water in the rooting zone as described in Marshall et al., this volume, pp. 22–60. The net precipitation remaining after these loss terms are removed may be delivered to the stream through a variety flow pathways as shown in Figure 11.1.

Channel precipitation

The most rapid precipitation contribution to streamflow is from precipitation that falls directly onto the channel or near-stream saturated areas, which can become incorporated directly and immediately into streamflow (channel precipitation) (Figure 11.1). Under most conditions, this term is generally small, since stream channels represent 1–2% of the total watershed area. However, as channels and saturated areas (where near-stream groundwater tables rise to and intersect the soil surface) expand during storms or seasonally, this contribution can increase and have major impacts on the chemical dilution of stream water. Channel precipitation can account for approximately 30% of stormflow in some watersheds and is typically highest (as a percent of total runoff) for low antecedent wetness conditions and low storm intensities (Crayosky et al. 1999) where runoff response ratios are low (i.e., where runoff divided by total storm precipitation is low).

Overland flow

Once the net precipitation reaches the soil surface it will move vertically into the soil at a rate less than the infiltration capacity and (under certain conditions) contribute to streamflow as a subsurface flow source (Figure 11.1). If the rainfall intensity exceeds the infiltration capacity of the soil, surface ponding will fill small depressions, which eventually connect to form rill-like sheets of overland flow (Smith & Goodrich 2005). Overland flow will continue and contribute as surface runoff as long as infiltration capacity is exceeded as the water moves over downslope soils; otherwise it infiltrates and becomes one of the subsurface flow paths shown on the right side of the Figure 11.1. This process was first described by Horton (1933) and is now termed Hortonian or infiltration-excess overland flow (although recent



papers have clarified Horton's perception of this and other runoff generating processes – see Beven (2004)). In most undisturbed forested ecosystems, the precipitation rate (e.g., a 25-yr return period storm for the southern USA is about 10 cm h^{-1} for a 1-h duration) rarely exceeds the infiltration capacity of soil (e.g. >20 cm h^{-1}) and therefore, the dominant flow paths are generally subsurface.

Subsurface flow may return to the surface and contribute to overland as groundwater exfiltration or seepage (Dunne & Black 1970; Eshleman et al. 1993). This is an overland-flow-producing effect but, unlike infiltration-excess overland flow (saturation from above), it is surface saturation from below. The area on the hillslope where this occurs will also receive direct precipitation onto pre-saturated areas developed from shallow water tables emerging at the soil surface, and together, return flow and direct precipitation onto saturated areas are termed saturation-excess overland flow (see (Anderson & Burt 1990) for detailed treatment and review of this process).

Subsurface flow

Subsurface flow processes are often considerably slower, more tortuous, and more difficult to discern than overland flow processes. First, we consider two major mechanisms that deliver subsurface water to streams: transport and displacement. Transport is defined as the movement of water according the pore water velocity field (Freeze & Cherry 1979). Therefore the physical processes of advection, diffusion, and dispersion affect water transport. Displacement, on the other hand, is much faster than actual flow velocities and can be characterized as the pressure propagation of precipitation rates through the saturated zone, which affects the discharge rate (Horton & Hawkins 1965; Beven 1989; Rasmussen et al. 2000). An example of the displacement or piston process is illustrated by considering water that enters a garden hose is not the same water that immediately exits the hose at the opposite end. Thus, in the watershed context, new rainfall may displace water to the stream, which previously had been stored in the soil mantle (Zimmermann et al. 1966).

We broadly separate subsurface flow into shallow and deep processes and consider the deep subsurface flow to be largely the groundwater flow component, i.e., saturated zone flow. However, saturated flow can also occur as shallow subsurface flow, sometimes called subsurface stormflow (e.g., perched water tables at the soil–bedrock interface or at some impeding horizon in the soil profile) (see the following section). We distinguish the shallow subsurface and deep subsurface flow processes based on depth and regional extent, where deep subsurface flow is thought to occur over a larger regional aquifer system. Groundwater flow is regarded primarily as flow through bedrock and/or confined to lowland areas (i.e., near stream) of a watershed such that it mimics the general topographic form of the drainage basin. Under driven conditions (i.e., during precipitation), groundwater may respond rapidly and contribute to streamflow via the piston-displacement mechanism, which is represented by the large dashed line within the subsurface runoff box in Figure 11.1. During non-driven periods, groundwater flow through bedrock, soils, and the near-stream zone sustains low flows through the dry season. Since water at depth, where soil permeability is often some orders of magnitude lower than the surface soil horizons, can only move slowly through connected pore space, outflow from groundwater may lag behind the precipitation episode by days, weeks, or even years.

In undisturbed forested watersheds in upland terrain, shallow subsurface flow often dominates the stream stormflow response. The specific processes that give rise to this component vary with climate, soils, and geology. At any particular location in the watershed, the initiation of shallow subsurface flow is highly dependent upon antecedent moisture conditions. Therefore, evapotranspiration (largely transpiration) exerts a major control on the generation of subsurface flow processes, mainly by establishing the initial moisture deficit necessary to overcome by removing water from the rooting zone. Shallow subsurface flow, which is often termed subsurface stormflow or throughflow, is very threshold dependent and describes the lateral movement (i.e., downslope) of water in the soil profile within the time frame of a storm hydrograph. There are numerous mechanisms ascribed to the formation of subsurface stormflow; however, in most cases, it represents a 'quickflow' pathway, meaning that it rapidly contributes to the formation of the hydrograph rise.

Shallow subsurface flow

Shallow subsurface flow processes have perplexed hydrologists since the early work of Hursh (1936, 1944) and to some extent are still ignored as a contribution to the storm event response. As mentioned above, overland flow is rarely observed in undisturbed upland watersheds; thus, hydrographs are largely composed of rapid subsurface flow and saturation-excess sources. The challenge has been in explaining how subsurface flow can so rapidly cause a streamflow response when measured soil matrix hydraulic conductivity data often contradict seemingly high soil water velocities. Observations have shown that two major processes give rise to rapid subsurface flow: (i) the rapid displacement of water stored in the watershed prior to the onset of precipitation, and (ii) preferential flow, mainly in the form of macropore flow. The displacement flow process, termed translatory flow by Hewlett & Hibbert (1967), suggests that streams can respond to rainfall inputs even though individual water molecules only travel centimeters or meters per day. This

process is most effective when soils are at or near saturation and is assisted by the frequently observed decrease in saturated hydraulic conductivity with depth in soil profiles (Taha et al. 1997; Buttle 1998). However, recent studies have indicated that pressure propagation in unsaturated soils causes a similar response (Torres et al. 1998; Williams et al. 2002) by the thickening of water films around soil particles and resulting in a water flux pulse as saturated conditions are approached (Hewlett & Hibbert 1967).

Water percolating vertically through the soil may encounter permeability decreases with depth (generally, the hydraulic conductivity decreases exponentially) that can cause localized areas of transient saturation (or near-saturation). When this happens in steeply sloping terrain, the gravitational component of the soil water potential causes flow vectors to move in a lateral direction, which might only occur briefly during storm events (Weyman 1973; Harr 1977; Torres et al. 1998). Lateral flow will increase as the soil approaches saturation because the hydraulic conductivity increases nearly exponentially with degree of saturation. As the saturated layer (i.e., perched water table) develops and extends upward in the soil profile into more transmissive soils, an additional water flux increase is often observed called the transmissivity feedback (Kendall et al. 1999; Bishop et al. 2004; Laudon et al. 2004). The development of lateral flow and transient saturation also is assisted by flow convergence in topographic and bedrock hollows (Beven 1978; Tsuboyama et al. 2000), along bedrock surfaces (Freer et al. 2002), and adjacent to bedrock exfiltration zones (Anderson et al. 1997; Uchida et al. 2003).

A rapid conversion from near-saturation (e.g., capillary fringe) to saturation can also occur in the soil profile when large inputs from rainfall or snowmelt combine with low effective porosity soils, yielding a disproportionately large and rapid rise in the water table (Abdul & Gillham 1984; Gillham 1984; Ragan 1968; Sklash & Farvolden 1979). This response occurs typically at the toe of the hillslope or near-stream zone and resembles a groundwater ridge or mound. The groundwater ridge induces locally steepened hydraulic gradients, which enhances groundwater discharge to the stream, and some studies have shown that the gradient on the other side of the mound is reversed back toward the hillslope (Bates et al. 2000; Burt et al. 2002). However, the applicability of the groundwater ridging mechanism has been questioned for soils with little capillary fringe development (i.e., coarse textured soils) (McDonnell & Buttle 1998). Soils that do develop a significant capillary fringe tend to have low saturated hydraulic conductivity, which conflicts with the hypothesis that it rapidly contributes to stormflow generation (Cloke et al. 2006).

Rapid flow through non-capillary soil pores (i.e., macropores) caused by root channels, animal burrows, cracks/fissures, or simply coarse textured or aggregated soils, is also frequently evoked as a major subsurface stormflow mechanism, especially in forested watersheds (Mosley 1979; Beven & Germann 1982; McDonnell 1990). Flow through macropores is conditional on saturation of the surrounding soil matrix or flow through the macropores exceeding the rate of loss to the surrounding matrix. Macropore flow and other preferential flow processes produced by wetting front instability (i.e., fingering) in unsaturated soils (Hill & Parlange 1972; Hillel 1998), cause accelerated movement of water to depth often bypassing portions of the soil matrix that can ultimately trigger a rapid conversion to saturated conditions at depth in the soil profile, where effective porosity is low compared with shallow soils (McDonnell 1990; Buttle & Turcotte 1999). Subsequently, the location of macropores and soil pipes (Jones 1971) that occur near the bedrock interface can enhance lateral drainage from hillslopes (Uchida et al. 2001).

Contributing source areas

The temporal and spatial nature of the aforementioned streamflow generation processes changes in response to antecedent moisture, precipitation intensity, and season, which are reflected by the varying extent of surface saturated areas produced in the watershed. This concept, which was introduced in the USA by Hewlett (1961) and simultaneously by Cappus (1960) in France and Tsukamoto (1961) in Japan, remains the major theoretical paradigm of streamflow generation. Saturated areas present an opportunity for the rapid conversion of rainfall to streamflow and thus are considered the primary contributing source area in a watershed. However, it is important to note that even though saturated areas expand and contract reflecting the storm response, those areas are not necessarily the only sources that actively contribute to stormflow (Ambroise 2004). Disjunct areas of the watershed must be hydrologically connected to organized drainage for some period of time to be considered a contributing source area. Connectivity may occur via surface saturated area development (Burt & Butcher 1985; Grayson et al. 1997), water table development (Stieglitz et al. 2003; Tromp-van Meerveld & McDonnell 2006), or by the generation of subsurface flow networks (Sidle et al. 2001). Often hydrologic connectivity is threshold driven such that a specific soil moisture state is needed prior to activating runoff from an area within the watershed (Bazemore et al. 1994; Grayson et al. 1997; Sidle et al. 2000; McGlynn & McDonnell 2003). Many observations have indicated that hillslope connections to near-stream zones also operate as thresholds requiring specific antecedent conditions prior to activation (McDonnell et al. 1998; Freer et al. 2002; McGlynn & McDonnell 2003). Recent work indicates that the threshold is not necessarily controlled by moisture status alone, but the depth to bedrock depressions, which fill to form transient saturated zones that connect and flow downslope depending upon event size and bedrock topography (Buttle et al. 2004; Tromp-van Meerveld & McDonnell 2006).

Why are stable isotopes needed?

Given the importance of overland and subsurface flow pathways to ecological processes (e.g. flushing of labile nutrients, etc), spatial and temporal resolution of these myriad pathways and processes is important. As Beven (1989) notes:

> . . . there is a continuum of surface and subsurface processes by which a hillslope [or watershed] responds to a storm rainfall, depending on the antecedent conditions, rainfall intensities, and physical characteristics of the slope and soil. . . . Individual storm responses may involve all of these processes [that we discuss above in this chapter] occurring in different parts of the same catchment, or different mechanisms occurring in the same part in different storms, or different times within the same storm.

It has been difficult to discern these processes using physical data alone. This is because the fluctuations in physical parameters, for instance groundwater levels, can arise from a variety of processes that can result in similar response patterns. In addition, many physical measures are point measurements and do not integrate hydrologic behavior to a scale that we are interested in such as a watershed or hillslope. Thus, other information is needed to help explain the movement and occurrence of water at more integrative scales.

Stable isotope tracers have been among the most useful tools employed to sort through Beven's surface–subsurface continuum to define the dominant runoff producing processes, geographic source of water comprising the storm hydrology, the time source separation of the flow response, and residence time of water in the subsurface. The next section of this chapter presents water stable isotope fundamentals as a starting point for how one might employ these techniques to resolve the age, origin, and pathway of runoff at the watershed scale.

General concepts in isotope hydrology

Isotope hydrology is based on the notion of tracing a water molecule through the hydrological cycle. Devine & McDonnell (2004) note that non-natural constituents have been widely used for centuries to characterize flowpaths and estimate ground water velocities. The Jewish historian Flavius Josephus recorded in approximately 10 CE that chaff was used as a tracer to link the spring source of the Jordan River to a nearby pond. More quantitative tracer tests using chloride, fluorescein and bacteria were employed in the large karst regions of Europe in the late 1800s and early 1900s (Devine & McDonnell 2004).

Stable isotopes of water (hydrogen (^{2}H or D for deuterium) and oxygen (^{18}O)) have been used since the pioneering work of Craig (1961). Unlike applied tracers, stable isotopes are added naturally at the watershed scale by rain and snowmelt events. These environmental isotopes (applied through meteoric processes) can be used to trace and identify different air and water masses contributing precipitation to a watershed since the stable isotope composition of water changes only through mixing and well-known fractionation processes that occur during evaporation and condensation. Once in the subsurface, and away from evaporative effects, the stable isotopes of water are conservative in their mixing relationships. This means that isotopic composition of the mixture of two water sources will fall on a straight line and its position is dependent only on the proportions of the two sources. Also, ^{2}H and ^{18}O, the elemental basis for H_2O molecules, are ideal tracers because they behave exactly as water would as it undergoes transport through a watershed. Water entering a watershed will have a characteristic fingerprint of its origin and therefore can help identify where the water in the stream comes from.

The isotopic composition of water is expressed as the ratio of the heavy to light isotopes (e.g., $^{18}O/^{16}O$) relative to a standard of known composition:

$$\delta \text{ (in ‰ or per mil)} = (R_x/R_s - 1) \times 1000 \qquad (11.2)$$

where R_x and R_s are the isotopic ratios of the sample and standard, respectively. The agreed upon standard issued by the International Atomic Energy Agency (IAEA) is Vienna-Standard Mean Ocean Water or VSMOW (Coplen 1996). The isotopic composition of water is determined by mass spectrometry (Kendall & Caldwell 1998).

Isotopic fractionation

Oxygen-18 and deuterium occur in water at abundances of 0.204% of all oxygen atoms and 0.015% of all hydrogen atoms, respectively (Clark & Fritz 1997). These relative abundances change slightly as a result of thermodynamic reactions that fractionate or partition atoms of different mass (isotopes vary in mass since they are defined as an element with the same number of protons, but different number of neutrons), which provides the unique isotopic composition indicative of the water source and process of formation. The isotopic fractionation in water occurs through diffusion during physical phase changes such as evaporation, condensation, and melt. Fractionation is strongly temperature dependent such that it is greater at low temperature (Majoube 1971). During phase changes, diffusion rates differ due to the differences in bond strength between lighter and heavier isotopes of a given element. Molecular bonds between lighter isotopes ($H_2{}^{16}O$) are more easily broken than molecular bonds between heavier isotopes ($HD^{16}O$ and $H_2{}^{18}O$).

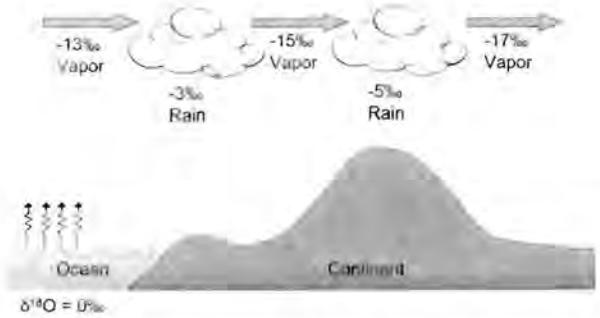


Figure 11.2 The diagram of isotopic composition of atmospheric water vapor over an ocean showing the processes of evaporation and rainout as the air mass proceeds over a continent. (Modified from Siegenthaler 1979.)

Heavy isotopic forms of water (i.e., with ^{18}O or ^{2}H) will require greater energy to break hydrogen bonds than water containing lighter isotopes and consequently, will react more slowly. For example, water vapor over large water bodies tends to be depleted in heavier isotopes (or enriched in lighter isotopes) relative to the evaporating water body (Figure 11.2). Stronger bonds indicate that heavy isotopic forms have lower saturation vapor pressures (i.e., the evaporation driving force) and thus, lower evaporation rates (i.e., diffusion across the water–atmosphere boundary layer). As the water vapor condenses from clouds to form precipitation, heavy isotopic forms will preferentially move into the liquid phase, which will be enriched in the heavy isotope compared with the residual water vapor. Under equilibrium conditions, the heavy isotopes are always enriched in the more condensed phases by an amount known as the fractionation factor, α. Further details of isotope fractionation can be found in Gat (1996), Kendall & Caldwell (1998), and Mook (2000).

Meteoric water line

The meteoric (or meteorological) water line (MWL) was first published by Craig (1961) and is a convenient reference for understanding and tracing water origin. It is a linear relation in the form of:

$$\delta D = 8\delta^{18}O + d \qquad (11.3)$$

where d, the y-intercept, is the deuterium-excess (or d-excess) parameter when the slope = 8 (Dansgaard 1964). Craig's MWL, referred to as the Global MWL, with $d = 10$ and a slope of 8, was based on approximately 400 samples representing precipitation, rivers, and lakes from various countries (Figure 11.3). Cold regions are associated with waters depleted in heavy isotopes and

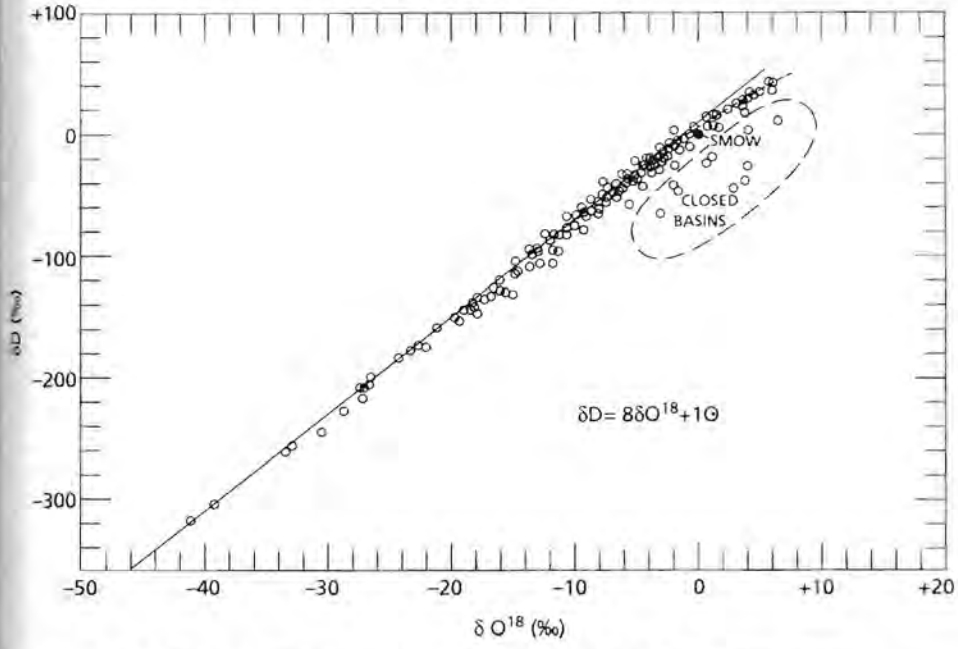


Figure 11.3 The global meteoric relationship between δD and $\delta^{18}O$ in water collected from rivers, lakes, rain, and snow by Craig (1961). Closed basins indicate areas where evaporation is significant and thus do not plot along the linear relation. Also, the dashed fit through the upper end of the data show enrichment of the heavy isotopes in samples collected from lakes in East Africa that experience evaporation effects. (Reprinted with permission from Craig, H. (1961) Isotopic variations in meteoric waters. *Science*, **133** (3465), 1702–1703. Copyright 1961 AAAS.)

warm regions tend to contain waters enriched in heavy isotopes (see Figure 11.4). The GMWL has been updated subsequently by (Rozanski et al. 1993) ($\delta D = 8.17\ (\pm 0.07)\ \delta^{18}O + 11.27\ (\pm 0.65)$ ‰) using weighted mean annual precipitation data from stations in the IAEA/World Meteorological Organization Global Network of Isotopes in Precipitation (GNIP). Local MWLs (linear $\delta D - \delta^{18}O$ relationships based on local precipitation measurements of at least a 1-year period) have been very useful for many water resource applications such as surface-water–groundwater interactions and evaporation effects. Local MWLs reflect variations in climate, rainfall seasonality, and geography by the deviations of the slope and d-excess value (see Figure 11.4). In most watershed studies, a LMWL would be constructed and used. Figure 11.4 shows that deviations from the GMWL can occur from humidity differences of the vapor source and from evaporation (as discussed later).

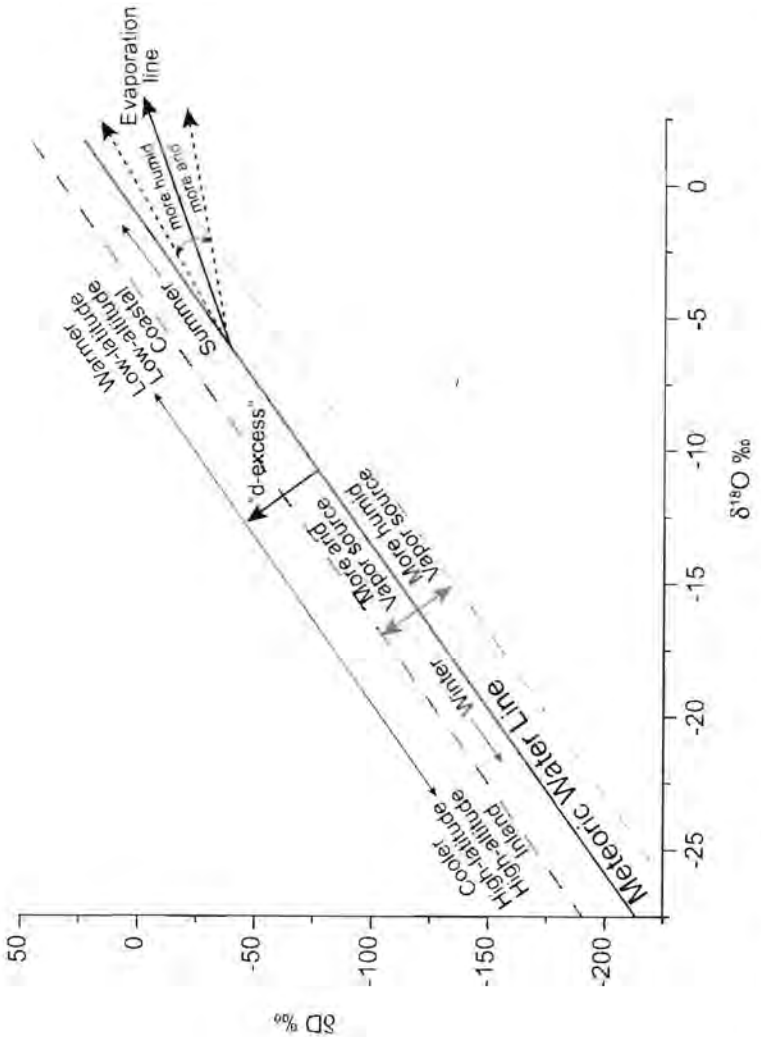


Figure 11.4 Schematic meteoric water line showing factors leading to deviations from the $\delta^{18}O$–δD relationship. (Modified after SAHRA 2005.)

Precipitation isotopic variation

An understanding of the processes that control the spatial and temporal distributions of precipitation isotopic composition is necessary since it is the ultimate source of water for all applications discussed in this chapter. Regional and global spatial distributions have been developed using interpolation schemes (Bowen & Revenaugh 2003) and atmospheric circulation models (Sturm et al. 2005), which help predict the isotopic input to watersheds. Temporal variations in the isotopic composition of precipitation have been used to evaluate climate change (Rozanski et al. 1992), recharge patterns (Winograd et al. 1998; Abbott et al. 2000), and residence time (Maloszewski et al. 1983; Pearce et al. 1986). The GNIP database contains stable isotope records for many sites around the world including spatial maps and animations of seasonal changes in the data for visualizing how precipitation stable isotope composition vary in time and space at the global scale (GNIP can be accessed from http://isohis.iaea.org/).

Precipitation has several so-called isotopic effects (or rules) that have been described and developed over the years and are useful to know for many of the watershed isotope tracing applications discussed in the following sections. The isotopic composition of precipitation is dependent upon several factors including the isotopic composition of its vapor source (typically from oceanic regions), fractionation that occurs as water evaporates into the air mass (sea-surface-temperature controlled), precipitation formation processes, and air mass trajectory (i.e., the influence of vapor source and rainout processes along the pathway of the air mass). Most of these factors are related to isotopic fractionation caused by phase changes.

As vapor masses form over ocean water, vapor pressure differences in water containing heavy isotopes impart disproportionate enrichments in the water phase during evaporation, which is dependent on sea surface temperatures (vapor pressure is higher for warmer regions such as equatorial regions), wind speed, salinity, and most importantly, humidity (Clark & Fritz 1997) (Figure 11.2). Rain will form from the vapor mass only through cooling that occurs from adiabatic expansion (no heat loss or gain) as warm air rises to lower pressures, or by heat loss through convection. Once the air cools to the dew point temperature, condensation and subsequent precipitation will occur and proceed to remove water vapor from the air mass. As the condensation temperature decreases, the δD and $\delta^{18}O$ values of precipitation also decrease. Then, as the system moves over continents, a rainout process causes the continual fractionation of heavy isotopes into the precipitation (i.e., according to a Rayleigh-like distillation, i.e., a slow process with immediate removal of the condensate) such that the residual vapor becomes progressively more depleted in heavy isotopes (Figure 11.2). Subsequent precipitation, while enriched with respect to the remaining vapor, will be depleted in heavy isotopes compared with previous precipitation from the same vapor

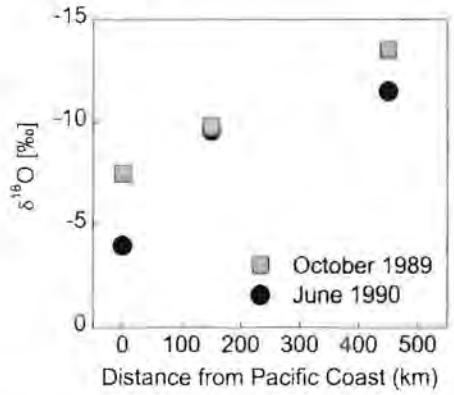


Figure 11.5 The $\delta^{18}O$ composition of precipitation (‰) collected during the first week of October in 1989 and during the second week of June in 1990 at three sites in Oregon: Alsea Guard Range Station, Andrews Experimental Forest, and at the Starkey Experimental Forest, which differ in their proximity to the Pacific Coast. (Modified after Welker 2000.)

mass (Clark & Fritz 1997). Of course, weather systems are not this simple, and are complicated by re-evaporation processes and atmospheric mixing with other vapor masses. Nevertheless, there are two major factors that control the isotopic composition of precipitation:

1 temperature (which controls the fractionation process);
2 the proportion of the original vapor that remains after the precipitation has begun.

Geographic and temporal variations associated with these factors are discussed below. They include the apparent effects of continental, elevation, amount, and latitude variations, which are due to temperature-dependent, continuous isotopic fractionation.

Continental effects

The process described above as rainout reduces the heavy isotopic composition of an air mass as it travels inland is known as the continental effect. Precipitation samples collected along a west to east transect in Oregon, USA (Figure 11.5) show a strong isotopic depletion in ^{18}O of approximately −1.5‰ per 100 km (Welker 2000), which is characteristic of the continental effect. Precipitation over inland temperate areas tends to be characterized by strong temperature variations (i.e., removed from moderating marine influences) and isotopically depleted precipitation with strong seasonal differences due to those temperature variations. Alternately, the isotopic composition of

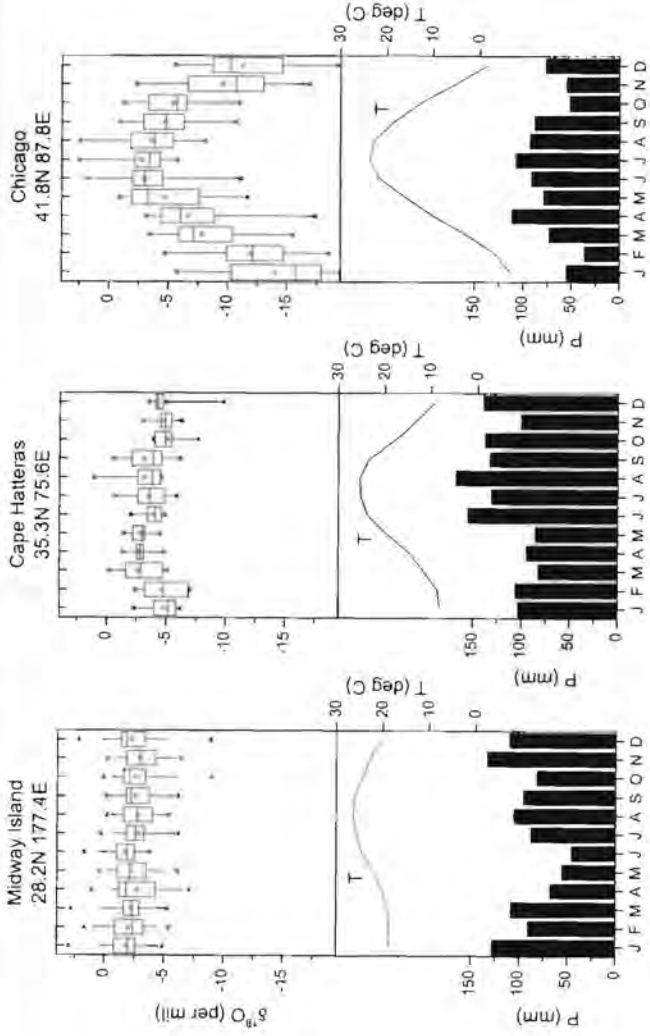


Figure 11.6 The seasonal variations in $\delta^{18}O$, temperature, and precipitation amount for Midway Island (a Pacific Ocean station), Cape Hatteras, North Carolina (an Atlantic coastal station), and Chicago, Illinois (A) (a continental station). The seasonal effect is more pronounced for continental sites with strong temperature variations. (Data are taken from the IAEA/WMO (2001) Global Network of Isotopes in Precipitation database.)

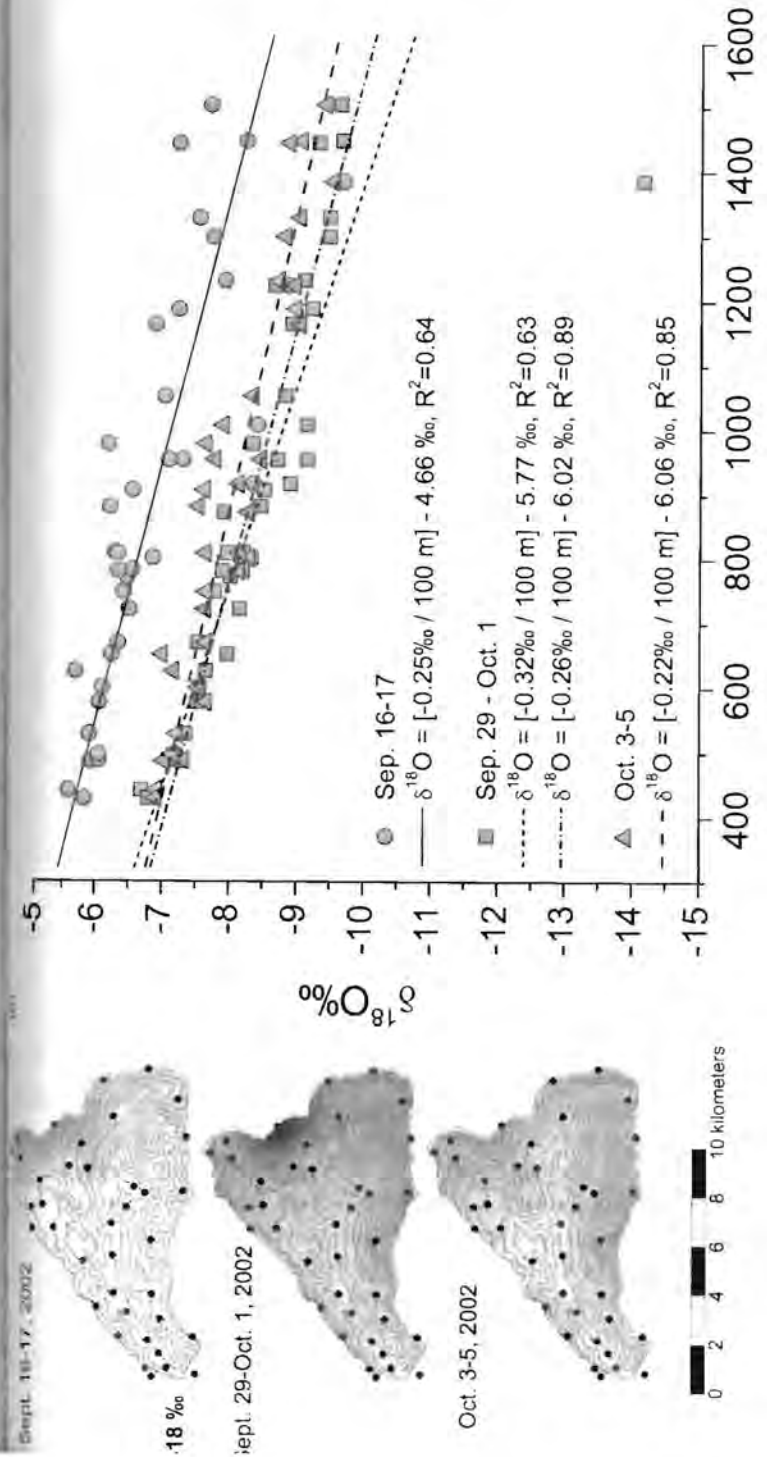
coastal precipitation tends to be less seasonally varied and isotopically enriched (Figure 11.6).

Pionke & DeWalle (1992) sampled 33 storms in central Pennsylvania and found that continental air masses originating from the Gulf of Mexico were generally less depleted than storms from oceanic air masses derived from the Atlantic. In addition, local storms that were not associated with frontal systems were the most depleted in ^{18}O. Celle-Jeanton et al. (2001) examined the typology of storms that affect the western Mediterranean region and found that based on 118 events, air masses originating from northern Atlantic and Mediterranean regions had very different isotopic compositions and rainfall amounts. Northern Atlantic storms had a strong continental effect since the air masses pass over Spain prior to reaching the monitoring station on the western Mediterranean coastline.

Elevation effects

Orographic precipitation caused by the cooling of air masses as they are lifted over higher elevation landforms, generally produces disproportionately higher rainfall with increased elevation on the windward side. This process forces rainout of heavier isotopic water; consequently, higher elevation regions receive more depleted precipitation. At higher elevations, isotopic depletion is further augmented by cooler average temperatures that cause increased fractionation. Gat (1980) suggests that secondary enrichment of raindrops resulting from partial evaporation during descent can contribute to the elevation effect. This process is dependent on the time raindrops are associated with unsaturated air, which is reduced in mountainous areas compared with valleys because raindrops fall shorter distances. Therefore, less enrichment of raindrops would be expected to occur in mountainous areas.

Observed elevation effects in the isotopic composition of precipitation have been reported in many studies around the world and generally vary from approximately −0.15 to −0.5‰ per 100 m increase in elevation and −1 to −4‰ per 100 m increase in elevation for ^{18}O and D, respectively (Clark & Fritz 1997). Detailed measurements in the western Cascades of Oregon showed that $\delta^{18}O$ from individual rainfall events were strongly elevation dependent (−0.22 to −0.32‰ per 100 m increase in elevation) and that elevation explained between 63 and 89% of the variance (Figure 11.7) (McGuire et al. 2005). The spatial pattern of these data suggests that elevation alone does not explain the isotopic variation in precipitation, but that other factors such as vapor source, air mass direction, and intensity (or amount) may affect the precipitation isotopic composition (Figure 11.7).



1.7 The variation of the ^{18}O composition in precipitation collected from three consecutive rain storms in the H.J. Andrews Experimental Forest, USA (area = 64 km^2). Both total rainfall amount (not shown) and $\delta^{18}O$ were highly correlated with elevation reflecting the amount and elevation addition to air mass trajectory (predominantly west to east). $\delta^{18}O$ and sampler elevation are plotted on the right with regression models fit to the s. Two models were fit to the September 29 – October 1 storm (squares): one with the high-elevation data point of −14.14‰ (slope = −0.32‰ nd one without that point (slope = −0.26‰ 100 m^{-1}).

Amount effects

Small rain storms are frequently observed to have more isotopically enriched water than larger storms. During brief rain showers, the amount effect has been attributed to evaporation and isotopic exchange of descending raindrops with atmospheric moisture, which more strongly affects storms of low rainfall intensity and low total rainfall amount (Dansgaard 1964; Gat 1980). As the storm proceeds, humidity beneath the cloud base increases through time, reducing the evaporation loss of the raindrops. The condensation of heavy isotopic forms early during larger rain events leaves subsequent rainfall with fewer heavy isotopes to acquire (Gedzelman & Arnold 1994). Thus, during longer duration rain storms, enrichment is less overall since evaporation is reduced in the later portion of the storm.

Latitude effects

Latitude effects are responsible for isotopic variations caused by cooler temperatures that air masses encounter as they proceed from equatorial regions, where 60% of the atmospheric vapor originates, to higher latitudes (Figure 11.8) (Yurtsever & Gat 1981). Condensation temperatures decrease which result in precipitation over higher latitudes having more negative isotopic composition. Rainout processes intensify this effect since polar regions (high latitudes) are situated at the end of the air mass trajectory where the isotopic-latitude gradient increases (Clark & Fritz 1997). The gradient over North America and Europe is approximately −0.5‰ per degree latitude for $\delta^{18}O$ (Yurtsever & Gat 1981). Once again, the animations of the GNIP data provide a very good visualization of the latitude effect (http://isohis.iaea.org/).

Intra-storm isotopic variations and throughfall

The initial isotopic composition of a rain event is heavy due to its formation by low altitude clouds and is typically followed by a gradual depletion in heavy isotopes, based on the amount effect, where the evaporation of raindrops below the cloud base is reduced over time as the air approaches saturation (Stewart 1975; Gedzelman & Arnold 1994) (Figure 11.9). As a storm progresses, the altitude at which rain is formed increases (i.e., due to frontal or convective rise), which decreases the air mass temperature and heavy isotopic composition of rainwater (Celle-Jeanton et al. 2004). Maximum depletion is usually achieved during the highest rainfall intensity which coincides with the maximum air mass cooling or lift, and is sometimes followed by an increase in heavy isotopic composition as the condensation altitude decreases, or by atmospheric mixing with a new air mass (Celle-Jeanton et al. 2004). This effect is shown in Figure 11.9. Other temporal patterns are common such as gradual depletion with no final enrichment and

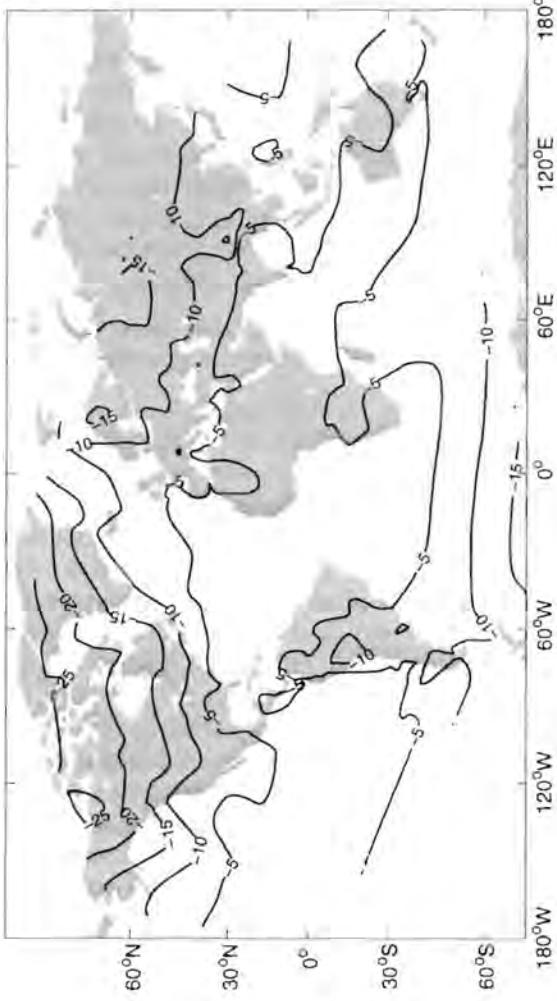


Figure 11.8 The global distribution of amount-weighted annual ^{18}O in precipitation based on 389 IAEA/WMO (2001) GNIP stations between 1961 and 1999 (created from data provided by Birks et al. 2002). These data illustrate the "latitude effect" where the isotopic composition of precipitation is lighter at higher latitudes. A simple cubic triangular interpolation was used for this map; however, more recent distribution maps have been created from the GNIP database using a Cressman objective analysis in a Grid Analysis and Display System (GrADS) (Birks et al. 2002), which includes monthly animations (see http://isohis.iaea.org) and using the Bowen–Wilkinson method (Bowen & Wilkinson 2001).

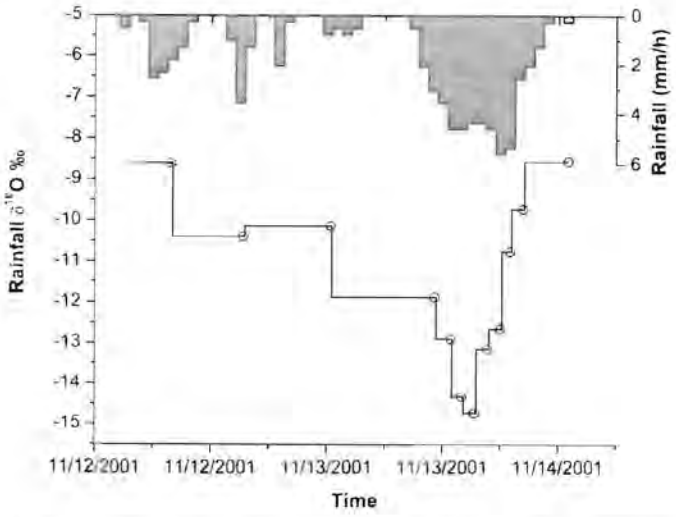


Figure 11.9 $\delta^{18}O$ temporal rainfall variations during a fall storm in the western Cascades of Oregon. The horizontal bars represent the time over which 5 mm rainfall increments were composited for each sample.

variations from mixing air masses related to successive frontal systems (McDonnell et al. 1990; Pionke & DeWalle 1992; Kubota & Tsuboyama 2003; Celle-Jeanton et al. 2004).

In many regions, gross precipitation is not the main isotopic input to the watershed; instead precipitation input to the soil surface is modulated by vegetation. In these instances, throughfall through the vegetation canopy and stemflow vertically down the stem (typically <5% of the annual rainfall) are the main inputs. Precipitation intercepted by the canopy is subject to evaporation and isotopic exchange with atmospheric vapor that leads to changes in the isotopic composition of rainwater (Gat & Tzur 1967; Saxena 1986) and snow (Claassen & Downey 1995; Cooper 1998). Throughfall is generally enriched in heavy isotopic forms (by approximately 0.5‰ and 3‰ for ^{18}O and D, respectively) through fractionation during evaporation and selective canopy storage for events with time-variable precipitation isotopic composition (Saxena 1986; Kendall & McDonnell 1993; DeWalle & Swistock 1994; Brodersen et al. 2000). Claasen & Dowy (1995) showed that intercepted snow enrichment can be much greater. They found that intercepted snow enrichments were about 2.1‰ and 13‰ for ^{18}O and D, respectively, according to results of a physically based model. The enrichment of intercepted snow was controlled primarily by the size of the snowfall and interception time.

As intercepted water evaporates from the canopy, fractionation (see above) processes usually lead to enrichment; however, molecular exchange with

atmospheric water vapor may result in depletion (Brodersen et al. 2000). DeWalle & Swistock (1994) showed that selective canopy storage was more important than fractionation in governing the throughfall isotopic composition. The process of selection is related to the time-variable nature of the isotopic composition of precipitation. It has been suggested that canopy storage (i.e., interception) of the rainfall from the end of a storm event, a time when rainfall is typically depleted in heavy isotopes, would be lost to evaporation and produce higher isotope contents for throughfall compared with rainfall. However, if rain is lighter at the beginning of the event, then throughfall would be depleted. Less intense and intermittent rain showers would exacerbate the selection process, since the opportunity for interception loss is greater and because these portions of the event comprise the most isotopically enriched rainfall (see 'Amount effect' above). Therefore, the understanding of canopy storage behavior is imperative in controlling the isotopic composition of throughfall – the main input to forested watersheds (Saxena 1986; DeWalle & Swistock 1994; and also see Keim & Skaugset 2004).

Snowmelt

The isotopic composition of the snowpack profile generally represents the distinct isotopic composition of individual precipitation events. In spite of this, isotopic exchange, combined with snowpack metamorphism and surface sublimation, attenuates the signal in the snow layers provided by the individual events (Cooper 1998). Snowmelt isotopic composition that develops from these snowpacks results from two major processes:

1 sublimation and molecular exchange between vapor and the snowpack;
2 meltwater infiltration and exchange with snow and vapor in the snowpack (Taylor et al. 2001).

The isotopic fractionation associated with sublimation of snow surfaces was shown by Moser & Stichler (1975) to behave similarly to that of evaporating water, except that the well-mixed conditions of a water body are not present in snowpacks (Cooper 1998). During initial snowmelt, meltwater is depleted in heavy isotopes relative to the snowpack; however, it progressively enriches throughout the snowmelt season as the snowpack isotopic composition becomes homogeneous due to the preferential melt of lighter isotopes (Cooper et al. 1993; Taylor et al. 2001; Unnikrishna et al. 2002). Figure 11.10 shows a time series of snowmelt input to a forest clearing at the Central Sierra Snow Laboratory near the crest of the Sierra Nevada from the onset of spring melt on March 1 to the disappearance of snow on May 1 (Unnikrishna et al. 2002). Snowmelt $\delta^{18}O$ inputs rapidly decreased from −9.15‰ to approximately −15‰ on April 9 illustrating the ^{18}O depleted snowmelt caused by the preferential concentration of heavy isotopes in the solid snow phase. During

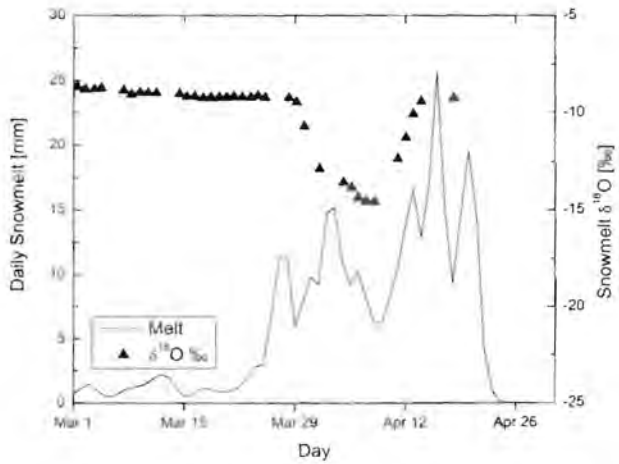


Figure 11.10 Daily snowmelt and snowmelt $\delta^{18}O$ from the Central Sierra Snow Laboratory, California. (Data from Unnikrishna et al. 2002.)

the final period of snowmelt, melt waters were progressively enriched in ^{18}O as the snowpack isotopic composition homogenized and resulting melt water increased to −9.20‰ on April 27 (Unnikrishna et al. 2002).

Applications of isotope hydrology in watershed and ecosystem studies

Evaporation rates

One direct application of stable isotopes in ecologically oriented studies is the calculation of evaporation. Since water isotopes fractionate upon phase changes, one can use isotopic enrichment during evaporation to estimate evaporation rates. This is a very simple and effective use of isotopes, used successfully by Gibson et al. (2002) for example, for computing lake surface evaporation in remote areas of northern Canada. Ambient humidity is the most important control on how evaporation from an open-water surface (or from a leaf surface or ponded water in a watershed) fractionates the isotopes of hydrogen and oxygen (Kendall & Caldwell 1998). Figure 11.11 shows that the higher the humidity during the evaporation process, the smaller the deflection from the meteoric water line in terms of change in $\delta^{18}O$ and δD during evaporation. For example, Figure 11.11 shows that at 95% humidity, the isotopic composition is constant for evaporation of the last 85% of the water. Evaporation results in lines with slopes <8 on a $\delta^{18}O$ vs. δD plot (i.e., the data plot on lines below the MWL that intersect the

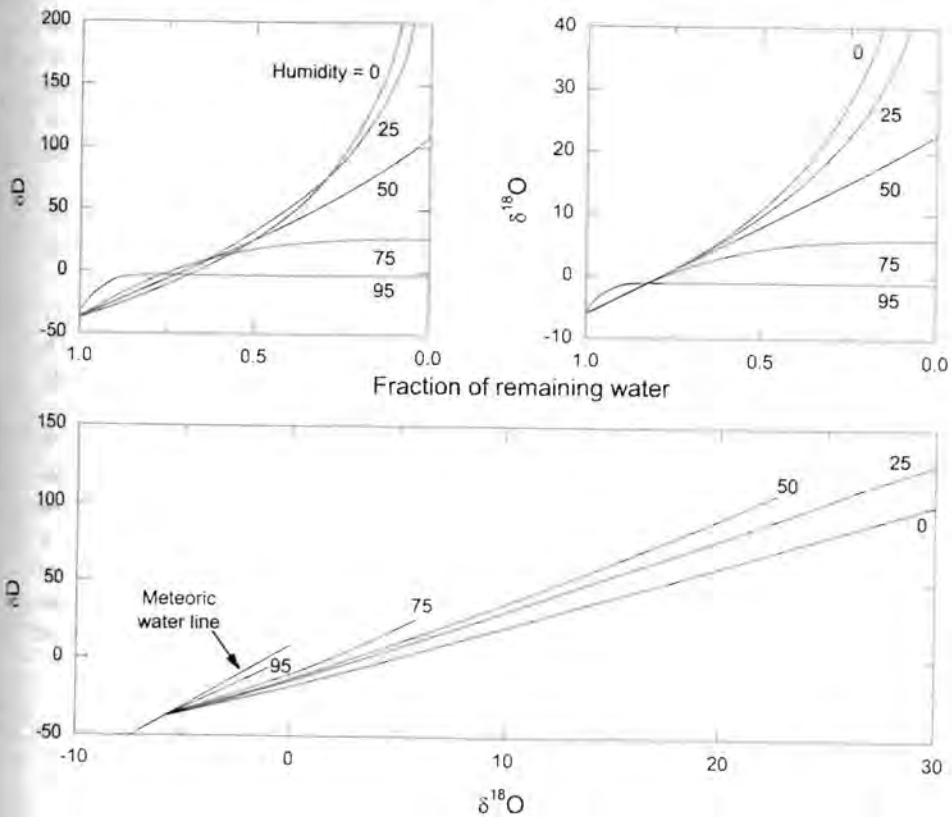


Figure 11.11 Humidity effects on $\delta^{18}O$ and δD of the residual water fraction during evaporation. Evaporation results in less fractionation at higher humidities and approaches a steady-state value for humidities >50% as the fraction of remaining water decreases. (Modified from Kendall & Caldwell 1998.)

MWL at the composition of the original water, see Figure 11.4) (Kendall & Caldwell 1998).

Lake evaporation as a fraction of precipitation can be calculated directly using the isotopic composition of a well-mixed lake that maintains a long-term constant volume (Gibson et al. 1993):

$$\frac{E}{P} = \frac{\delta_P - \delta_L}{\delta_E - \delta_L} \tag{11.4}$$

where E is lake evaporation, P is precipitation, δ_P is the weighted mean isotopic composition of local precipitation, δ_L is the isotopic composition of lake water, and δ_E is the isotopic composition of the evaporative flux. Values of δ_P and δ_L can be obtained readily by sampling precipitation and lake

water; however, δ_E cannot be directly sampled. Estimates of δ_E are possible through calibration with a nearby lake of known water balance (Dinçer 1968), from pan evaporation experiments (Welhan & Fritz 1977), or from theoretical models (Craig & Gordon 1965) that require estimates of the isotopic composition of atmospheric vapor (δ_A). The Craig and Gordon model of δ_L is:

$$\delta_L = \frac{\delta_L - h\delta_A - \varepsilon}{1 - h + \varepsilon_K} \tag{11.5}$$

where h is the relative humidity normalized to the saturation vapor pressure at the temperature of the lake surface water–air interface and ε is the total isotopic enrichment factor, which accounts for both equilibrium ε^* and kinetic ε_K enrichment. Relative humidity and δ_L can be directly measured and ε^* is well-known for ^{18}O and ^{2}H as a function of temperature and ε_K is understood from theoretical and experiment studies (e.g., Merlivat 1978). The value of δ_A has been estimated by assuming that atmospheric vapor is in isotopic equilibrium with local precipitation (i.e., $\delta_A = \delta_P - \varepsilon^*$, and ε^* is approximated using mean air temperature), which generally holds if the slope of a local evaporation trend (see Figure 11.4) can be shown to be independent of h (Gibson et al. 1999). Equation 11.4 and 11.5 can then be combined as:

$$\frac{E}{P} = \frac{1-h}{h}\frac{\delta_L - \delta_P}{\delta^* - \delta_L} \tag{11.6}$$

where δ^* is:

$$\delta^* = \frac{h\delta_A + \varepsilon}{h - \varepsilon} \tag{11.7}$$

Estimates of lake evaporation using equations 11.6 & 11.7 are best suited for longer-term studies involving complete annual cycles (Gibson et al. 1993, 1996).

Hydrograph separation

Hydrologists have traditionally separated the streamflow response (i.e., the discharge hydrograph) to rainfall and snowmelt inputs into its component parts using graphical techniques. Beyond the simple and rather arbitrary graphical measures used in engineering hydrology for channel routing and storm water drainage, other methods such as those introduced by Hewlett & Hibbert (1967), separate streamflow into "runoff components" (i) quickflow and (ii) delayed flow. Quickflow has been used frequently as a measure to describe the responsiveness of the watershed to a storm event. The term delayed flow is synonymous with baseflow (i.e., the flow in the stream

between events) and conceptually represents the sum of the delayed shallow subsurface flow through the soil mantle and deep subsurface flow of groundwater (Ward & Robinson 2000). However, neither quickflow nor baseflow can be equated directly to precipitation–runoff conversion processes. While used extensively in watershed studies (Bonell, 1998), the quickflow separation method is still rather arbitrary for defining the relative rates of flow and neither it nor the engineering based approaches allow for the calculation of the geographic or time source of water contributing to streamflow.

Hydrograph separation has been perhaps the main use of environmental isotopes to date in small watershed hydrology (see reviews in Genereux & Hooper 1998; Rodhe 1998; Buttle & McDonnell 2004). Early isotopic hydrograph separations (IHS) used tritium (^{3}H) (Martinec 1975), but most studies in the past 25 years or so have used oxygen-18 (^{18}O) and deuterium (^{2}H) (Genereux & Hooper 1998; Burns 2002). Unlike ^{3}H, ^{18}O and ^{2}H are stable and do not undergo radioactive decay. Unlike the engineering approaches and the Hewlett & Hibbert approach, IHS can aid in quantifying the time source of water components of the storm hydrograph. When combined with additional tracers, IHS can also help to quantify the geographic source of water contributing to the hydrograph (Ogunkoya & Jenkins 1993).

Isotope tracers have a number of very useful attributes as water tracers for hydrograph separation (Buttle 1994).

1 They are applied naturally over entire catchments (unlike artificial tracers where application rates and extent are limited).
2 They do not undergo chemical reactions during contact with soil/regolith at temperatures encountered in the subsurface of watersheds.
3 New water is often different to old water. Numerous studies have shown that variations in the isotopic signature of precipitation are dampened as water transits the unsaturated zone to the water table (Clark & Fritz 1997). Groundwater isotopic composition may approach that of the mean annual precipitation isotopic values. In areas where seasonal isotopic variations in precipitation exist (e.g. middle and northern latitudes), there is frequently a difference between the isotopic composition of water input to the catchment's surface and water stored in the catchment before the event.

This difference between the isotopic signature of incoming water (event or "new" water) and water stored in the catchment before the event (pre-event or "old" water) often permits the separation of a stormflow hydrograph into a two-component mixing model: event and pre-event:

$$Q_t = Q_p + Q_e \tag{11.8}$$

$$\delta Q_t = \delta_p Q_p + \delta_e Q_e \tag{11.9}$$

$$X = (\delta_t - \delta_p)/(\delta_p - \delta_e) \tag{11.10}$$

where Q_t is streamflow; Q_p and Q_e are contributions from pre-event and event water; δ_t, δ_p and δ_e are isotopic compositions of streamflow, pre-event and event waters, respectively; and X is the pre-event fraction of streamflow. Event water is typically sampled in bulk or incrementally during storms and weighted by volume in the mixing model (equation 11.10). McDonnell et al. (1990) evaluated three weighting methods to determine the event water composition and found that incremental averaging methods were best for handling the temporal variability of the rainfall isotopic composition. Many of these methods assume an instantaneous mixing with pre-event water to produce the stream isotopic content at any time during the storm event; however, some recent studies have included delays or travel time distributions for the event water term in the mixing relationship shown in equation 11.10 (Joerin et al. 2002; Weiler et al. 2003).

The IHS results generally show that over half (more typically about 75%) the runoff and/or peakflow associated with rain storms is composed of pre-event water (Genereux & Hooper 1998). However, as Burns (2002) notes, most of our studies have focused on humid, temperate forested watersheds and little information is available for semi-arid and urban watersheds (see Buttle et al. 1995; Newman et al. 1998; Gremillion et al. 2000).

New techniques that combine simple rainfall–runoff models and IHS have made it possible to learn more about runoff generation processes than the use of the mixing model alone (Weiler et al. 2003; Iorgulescu et al. 2005). For example, Weiler et al. (2003) combined a transfer function model of the hydrology with an isotopic mixing model (equation 11.10) and were able examine the response time distributions of new water inputs (i.e., new water residence time) to a watershed for different storms and explore possible runoff generation processes.

Recharge rates and source

Given the clear and unambiguous signal of waters that have undergone evaporation (see above), quantifying recharge sources can be done quickly, clearly, and effectively with stable isotope tracers (Burns & McDonnell 1998). A simple and still relevant example was presented by Payne (1970) who illustrated how one could define sources of water recharge to springs around Lake Chala for basic water resources development questions. Here, villagers wanted to know if they could use water from Lake Chala for irrigation. They were mindful of the fact that using lake water could have a negative impact on flow from nearby springs used for drinking water supply if in fact the lake water recharged the springs. Payne (1970) shows a very clear example where plotting precipitation, lake water, and spring water on a meteoric water line can help reject possible recharge sources and connections (Figure 11.12). In this case, spring water plots on the meteoric water line and the lake waters

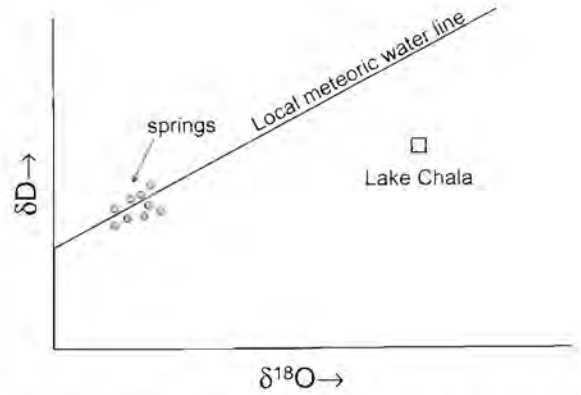


Figure 11.12 Lake Chala (square) and samples from a near-by spring (circles) plotted on the local meteoric water line. The figure is redrafted from a diagram of C. Kendall, as interpreted from the Payne (1970).

plot below the line indicating that lake water did not recharge the springs. If it did, the spring water would also plot off the MLW. The clear and unambiguous evaporation signal of the lake was very helpful in determining the lack of a groundwater and surface water connection.

Water travel time

Stable isotopes can be used as tracers to estimate how long it takes for water to travel through a watershed (Maloszewski & Zuber 1996; McGuire 2005; McGuire & McDonnell 2006). The travel time or residence time of water has important implications for water quality and the persistence of contaminants in the environment. Longer residence times indicate greater contact time and subsurface storage implying more time for biogeochemical reactions to occur (Scanlon et al. 2001; Burns et al. 2003).

Strong correlations between seasonally varying tropospheric temperature variations and the stable isotope composition in meteoric water provide an input isotopic signal that can be used in conjunction with the isotopic signal in a stream to estimate travel times. Estimating the distribution of travel times in a watershed using stable isotopes requires a well-monitored precipitation isotopic signal that should exceed at least 1 year; however, longer signals (>5 years) provide more reliable results (McGuire & McDonnell 2006). In addition, an input function is required to correct the precipitation isotopic composition to represent the recharge isotopic flux (Maloszewski et al. 1992; Vitvar & Balderer 1997; McGuire et al. 2002).

Water travel time distributions for catchments are typically inferred using lumped parameter models that describe integrated transport of

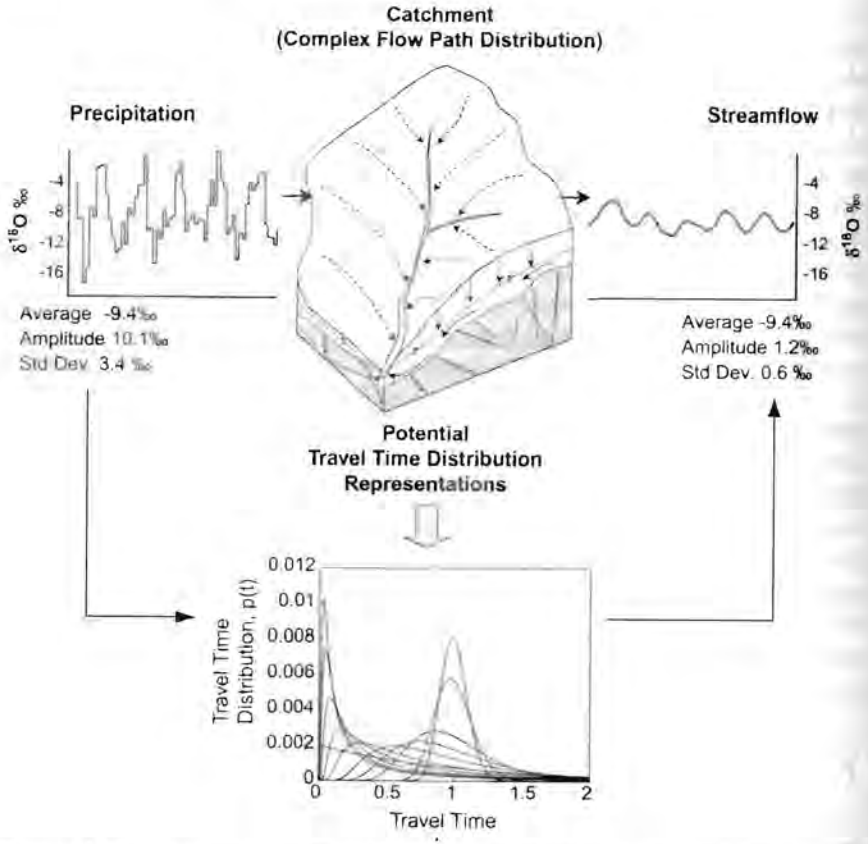


Figure 11.13 Conceptual diagram of the lumped parameter travel time modeling approach. Catchments receive $\delta^{18}O$ inputs that are transported along diverse flow paths in the unsaturated and saturated zones as the isotopes migrate through the subsurface toward the stream network. The result of differential transport within the catchment is an output streamflow $\delta^{18}O$ signal that is damped (i.e., decrease in standard deviation and amplitude) and lagged compared with the input signal. The complex distribution of catchment flow paths is represented by a distribution of travel times, $p(t)$, that describe the integrated behavior of tracer transport through the catchment. (Modified from McGuire & McDonnell, 2006.)

the isotopic tracer through a catchment's subsurface via system response functions. Figure 11.13 illustrates the lumped parameter modeling approach for estimating the travel time distribution of water draining a catchment. The isotopic composition of precipitation that falls over the entire watershed area is transported to the stream network along diverse flow paths within the subsurface environment (see discussion of streamflow generation at the beginning of the chapter). The transport process along these diverse subsurface flow paths causes time delays (due to advection and dispersion)

of precipitation isotopes as they arrive at the stream network, which is a direct manifestation of the catchment's flow path distribution, runoff processes, and subsurface hydrologic characteristics. The integrated response of isotopic arrival at the catchment outlet from all locations in the catchment is described by the travel time distribution (i.e., a probability density function of travel times). This process can be mathematically expressed by the convolution integral, which states that the stream isotopic composition at any time, $\delta_s(t)$, consists of precipitation with a unique isotopic signal, $\delta_p(t-\tau)$, that fell uniformly on the catchment in the past, which becomes lagged according to its travel time distribution, TTD(τ) (Maloszewski & Zuber 1982; Barnes & Bonell 1996; Kirchner et al. 2000):

$$\delta_s(t) = \int_0^\infty TTD(\tau)\delta_p(t-\tau)d\tau \tag{11.11}$$

where τ are the lag times between precipitation and streamflow isotopic composition. A catchment's TTD could have various shapes depending on the exact nature of its flow path distribution and flow system assumptions. Equation 11.11 is only valid for the steady-state and when the mean subsurface flow pattern does not change significantly in time; however, it may be suitable for catchments where flow parameters (e.g., velocity) do not deviate significantly from the long-term mean values and when the water table fluctuations are small compared with the total subsurface volume (Zuber 1986).

The TTDs in equation 11.11 are typically composed of simple (i.e., one to three parameters) response functions that conceptually represent the dominant pathways, storages, and flow conditions of the real system. These TTDs can take the form of exponential flow reservoirs, piston-flow systems, exponential flow systems in parallel or series, and dispersive flow systems (Maloszewski & Zuber 1996; Turner & Barnes 1998). There has also been some evidence that the catchment geometry and topographic organization may exert some control on the shape of the catchment-scale TTD (Kirchner et al. 2001; McGuire et al. 2005). In current practice, TTDs are selected based either on an assumed flow system (Maloszewski & Zuber 1982) or through a fitting exercise resulting from numerous model simulations. This can be problematic since parameters are often not identifiable and different model types can yield non-unique results (Maloszewski & Zuber 1993). A full discussion on TTD models is beyond the scope of this chapter; however, there are many examples of the use of these models for catchment and groundwater systems (Stewart & McDonnell 1991; Vitvar & Balderer 1997; Buttle et al. 2001; McGuire et al. 2002).

Diagnostic tools in models

While this chapter has shown the usefulness of stable isotope approaches for understanding watershed function, very few studies have yet incorporated

tracer data, interpretations, and concepts into current catchment-scale hydrologic models. The view that one's model captures the real-world processes correctly if one "fits" the hydrograph correctly still persists, but Hooper (2001, p. 2040) notes that "agreement between observations and predictions is only a necessary, not a sufficient, condition for the hypothesis to be correct." Seibert & McDonnell (2002) have argued that the experimentalist often has a highly detailed, yet highly qualitative, understanding of dominant runoff processes – and thus there is often much more information on the catchment than we use for calibration of a model. While modelers often appreciate the need for "hard data" for the model calibration process, there has been little thought given to how modelers might access this "soft data" or process knowledge, especially that derived from isotope tracer studies. Seibert & McDonnell (2002) presented a new method where soft data (i.e., qualitative knowledge from the experimentalist that cannot be used directly as exact numbers) are made useful through fuzzy measures of model-simulation and parameter-value acceptability. They developed a three-box lumped conceptual model for the Maimai catchment in New Zealand, where the boxes represent the key hydrological reservoirs that are known to have distinct groundwater dynamics, isotopic composition, and solute chemistry. The model was calibrated against hard data (runoff and groundwater-levels) as well as a number of criteria derived from the soft data (e.g. percent new water from isotope hydrograph separations). They achieved very good fits for the three-box model when optimizing the parameter values with only runoff ($E = 0.93$; E is the Nash & Sutcliffe (1970) efficiency, where 1 is a perfect fit). However, parameter sets obtained in this way in general showed a poor goodness-of-fit for other criteria such as the simulated new water contributions to peak runoff. Inclusion of soft-data criteria in the model calibration process resulted in lower E values (around 0.84 when including all criteria) but led to better overall performance, as interpreted by the experimentalist's view of catchment runoff dynamics. The model performance, with respect to the new water percentage, increased significantly and parameter uncertainty was reduced by 60% on average with the introduction of the soft data multi-criteria calibration. This work suggests that hydrograph separation information may have new applications in model calibration, where accepting lower model efficiencies for runoff is 'worth it' if one can develop a more 'real' model of catchment behavior based on the information content of the isotope approach. More recent work has suggested that these approaches can be useful for other model structures and other model applications (Vaché et al. 2004).

Conclusions

Watershed hydrology is a field of study very much related to ecology. Questions of where water goes when it rains, what flowpaths the water takes to the stream, and how long water resides in the watershed underpin many questions of plant water availability, biogeochemical cycling, microbial production, and other water-mediated ecological processes. Stable isotope tracing and analysis forms an important link between hydrologic and ecological processes at the watershed scale where knowledge of flow path, water source and age inform many water mediated ecological processes. We have tried to illustrate in this chapter how an understanding of watershed hydrology can be used to better understand water quality, sustainability, land-use change effects, nutrient cycling, and general terrestrial and aquatic system interactions via isotope-based techniques. The potential for future studies to explore the interface between hydrology and ecology using isotopic techniques is very positive.

Acknowledgments

We would like to express our appreciation to Carol Kendall for many useful discussions over the years. Her collaboration and insight on many projects has been an encouraging influence to us. We continue to draw upon her wide expertise in isotope biogeochemistry and hydrology and make use of some examples she features in her U.S. Geological Survey short course in this chapter. We also thank the editors for their comments and patience, and for inviting us to contribute to this second edition.

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