Chapter 10

Oxygen and Hydrogen Isotopes in Rainfall-Runoff Studies

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10.1 Introduction

Knowledge of the hydrologic pathways by which water moves over and through the ground to streams represents an important component of our hydrological, geochemical, and ecological understanding of the Earth's surface. Streamflow generation (the drainage of water to streams and rivers) is a key component of the hydrologic cycle, and as such it is of fundamental scientific interest in itself. In addition, as in most areas of hydrology, there are areas in which fundamental scientific knowledge can be applied for the benefit of society and the environment. For example, a thorough understanding of streamflow generation can clearly be useful in designing computer models for streamflow prediction, and predicting streamflow is of importance in land use planning, flood contingency planning, and dam construction and operation. Also, the nature of water storage and drainage on hillslopes has important implications for slope stability, erosion, and related aspects of geomorphology. Finally, prediction of the chemical impacts of non-point source pollutants also requires an understanding of the pathways through which water moves on its way to the stream, because different pathways provide different opportunities for contact with organic detritus, soil, and rock. For example, the chemistry of water in an organic surface soil may be very different from that of water in the underlying mineral soil (e.g., Hooper et al., 1988), and both may be very different still from water in the local bedrock (e.g., Mulholland, 1993; Genereux et al., 1993). For these and other reasons, the field study of streamflow generation remains a significant topic in hydrology.

Naturally-occurring stable isotopes of oxygen and hydrogen are among the most effective tools available for delineating and constraining hydrologic flowpaths on watersheds. The basis for this application of $\delta^{18}O$ and δD is the temporal variation in the isotopic composition of precipitation. It is well known that the isotopic composition of rainfall varies from storm to storm at a given site (e.g., Pionke and DeWalle, 1992; Chapter 3); thus, the rainfall in any one storm may differ isotopically from the water stored in the subsurface at the start of the storm. This contrast in isotopic composition has proved useful in analysis of streamflow generation on storm event time-scales. The isotopic composition of precipitation also varies with season, leading to a variation of the isotopic composition of streamwater on this longer time-scale as well. This chapter seeks to provide an overview of traditional hydrograph separation applications on storm event time-scales. Beginning with an introduction to terminology and assumptions inherent to hydrograph separation, we will address the requirements for successful separation and discuss the results of several isotopic hydrograph separation studies. We

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conclude by considering other frameworks for application of isotope data, on storm-event and longer time-scales.

10.2 Hydrograph Separation

10.2.1 Terminology

Two-component hydrograph separation provides the simplest means (conceptually and computationally) for use of oxygen and hydrogen isotopes in analysis of streamflow generation. Sklash et al. (1976) and Sklash and Farvolden (1979) provide a simple, logical, and widely-used framework for the relationship between isotopic and other types of hydrograph separations. As Sklash et al. (1976) wrote: "Storm runoff in a stream consists of a number of component parts, which may be categorized in three ways: *time source* components, *runoff mechanism* components, and *geographic source* components". Event and pre-event water are the time source components of isotopic hydrograph separation. Event water refers to rain falling and/or snow melting during a storm and/or melt event of interest, whereas pre-event water refers to liquid water present on the watershed before the start of the event of interest. More recently the terms "new water" and "old water" have come into use as synonyms for event and pre-event water, respectively (Obradovic and Sklash, 1986; Pearce et al., 1986; Sklash et al., 1986; Hooper and Shoemaker, 1986). However, the terms "event" and "pre-event" are somewhat preferable in that they are more explicit and they serve as a reminder that the time source separation may be applied only to rain and/or snowmelt events, and not to baseflow between events.

Returning to the framework of Sklash et al. (1976), and modifications in Sklash and Farvolden (1979), each "runoff mechanism" component represents water arriving at a stream through operation of one of the physical mechanisms described in the streamflow generation literature (see Chapter 1), such as Hortonian overland flow, variable source area overland flow (or saturation overland flow), groundwater flow, or perched saturated flow. "Geographic" (or what was renamed "historical" in the 1979 paper) source components are somewhat less well-defined, but generally distinguish among different possibilities for where the water was located before arriving at the stream (e.g., in the saturated zone or in the vadose zone).

This general framework is a useful starting point for investigation of streamflow generation with isotopic data. Strictly speaking, a two-component isotopic hydrograph separation yields the proportions of event and pre-event water in a stream, nothing more. Because it is runoff mechanisms (or in some cases, geographic sources) which are of more fundamental significance in watershed hydrology, finding meaningful relationships between these components and time source components (event and pre-event water) has been and remains one of the fundamental priorities in extracting as much hydrologic information as possible from isotopic data. As is discussed in Section 10.2.3, relationships between time source and other components have often been built around quasi-quantitative observations or arguments concerning physical characteristics of a particular study site. In any case, it is important to bear in mind that isotopic data do not necessarily distinguish, for example, groundwater (a geographic source component) and new water (a time source component); as Genereux and Hemond (1990) point out, "not all old water is groundwater and, during and after storms, not all groundwater is old water."

10.2.2 Requirements and assumptions in hydrograph separation

Oxygen or hydrogen isotopes may be used to separate a hydrograph if the difference in the isotopic compositions of event and pre-event waters is "large" relative to the isotopic variability within each component and the analytical uncertainty associated with the isotopic analyses (the same general condition could be stated for any mixing problem involving use of a tracer). The requirement for a "large" difference in isotopic composition between event and pre-event waters is not specified in quantitative fashion here, because it depends on the amount of uncertainty one is willing to incur in the final hydrograph separation results (see Section 10.2.5). Most authors that have addressed the requirements for successful hydrograph separation have listed specific criteria rather than the general condition given above. For example, according to Sklash and Farvolden (1979), successful isotopic hydrograph separation requires that:

1. The isotopic content (^{18}O, D, T) of the event component is significantly different from that of the pre-event component.
2. The event component maintains a constant isotopic content.
3. The groundwater and vadose water are isotopically equivalent or vadose water contributions to runoff are negligible due to hydrogeologic constraints.
4. Surface storage contributes minimally to the runoff event.

(D and T in item 1 refer to ^2H and ^3H, respectively.) Item 1 in this list obviously states the requirement for an isotopic difference between event and pre-event waters. The other items refer to intra-component isotopic variability, specifically the requirements that the isotopic composition of event water not vary with time and that the composition of pre-event water not vary in space or, if it does, that only one pool of pre-event water (e.g., groundwater and not vadose zone water or surface storage) contribute significantly to storm runoff.

Failure to meet all of the requirements for successful separation is one of the main drawbacks of isotopic hydrograph separation. Event and pre-event waters are often too similar in composition, and one or the other may exhibit significant internal variability (see Section 10.2.4). Another limitation of the technique is that it may be applied only to stormflow. The major strength of the technique is that stream isotope data offer a watershed-scale signal that is linked to hydrologic pathways. Like the rate of streamflow itself, the isotopic composition of streamwater is an integrated signal responsive to streamflow generation processes in the watershed upgradient of the stream measurement point.

10.2.3 Findings

General Result

Table 10.1 summarizes the findings from a number of studies in which oxygen and/or hydrogen isotopes were used to separate storm streamflow into pre-event and event water. Table 10.1 includes only studies which focused on analysis of precipitation events; studies aimed at snowmelt and combined snowmelt-plus-precipitation events are considered in Chapter 11. Also excluded from Table 10.1 are studies in which hydrograph separations were not computed though isotopes were applied in a descriptive fashion (e.g., Kennedy et al., 1986) or in some other quantitative framework (e.g., Turner and Macpherson, 1990). Many studies in Table 10.1 present graphical examples of hydrograph separation results, as in Figures 10.1 and 10.2.

Table 10.1. Each value in the column labeled "volume" is a volume-weighted average percentage of pre-event water over the hydrograph; values in the column labeled "peak" refer to peak flow, except for two studies (Bottomley et al. (1984) and Mook et al. (1974)) which reported the minimum percentage of pre-event water for the hydrograph (i.e., 100 minus the peak in event water percentage). * indicates summary data were taken from Table 1 of Jordan (1994), not from the original paper. Some of these studies could have involved snowmelt, though this is not specifically indicated in any of the titles. For studies reporting more than two values for a given watershed, the table contains the lowest and highest values separated by a hyphen. Watershed areas shown as approximate for Sklash et al. (1976) were estimated by the present authors using a map in the original paper. For Bonell et al. (1990), values were calculated from Q_0 and Q_n data in their Table IV and taken from p. 31 of the text.

Study	Location	Catchment area (ha)	Tracer	Percentage pre-event water	
				peak	volume
Jordan (1994)	Switzerland	3.6	^{18}O		45, 75
Waddington et al. (1993)	Ontario	160	^{18}O	87, 93	
McDonnell et al. (1991)	New Zealand	3.8	D	92-100	
O'Gunkoya & Jenkins (1991)*	United Kingdom	1000	D		54-90
McDonnell et al. (1990)	New Zealand	310	D		21-33
Nolan and Hill (1990)	California	1060	D		57
Bonell et al. (1990)	New Zealand	218	D		59
		310	D	38	38 to >97
Blowes and Gillham (1988)	Ontario	0.75	^{18}O	9, 45	22, 50
Turner et al. (1987)	W. Australia	82	^{18}O, D		69-95
Herrman et al. (1987)*	Germany	76	^{18}O		84
Rodhe (1987)	Sweden	3	^{18}O		81, 87
		4	^{18}O		81, 96
		17	^{18}O	87	
		50	^{18}O		85-99
		400	^{18}O		68-86
		660	^{18}O		75-95
Pearce et al. (1986)	New Zealand	3.8	^{18}O		≥97
Sklash et al. (1986)	New Zealand	3.8	D		73-79
		1.6	D		74, 86
Bottomley et al. (1984)	Ontario	41.8	^{18}O	85-90	
		124	^{18}O, D		~40
		176	^{18}O	70-88	
Merot et al. (1981)*	France	10	^{18}O		88
Sklash & Farvolden (1979)	Quebec	120	^{18}O	>65, >80	

Table 10.1. Continued.

Study	Location	Catchment area (ha)	Tracer	Percentage pre-event water	
				peak	volume
		390	^{18}O	>80	
	Ontario	100	^{18}O	>80 (two)	
Sklash et al. (1976)	Ontario	~70,000	^{18}O	70	
		~40,000	^{18}O	71	
		~10,000	^{18}O	55	
		~35,000	^{18}O	69	
		~17,000	^{18}O	52	
		10,800	^{18}O	70	
		7300	^{18}O	75	
Fritz et al. (1976)*	Canada	180	^{18}O		45
		2200	^{18}O		60
		13,500	^{18}O		>50
Mook et al. (1974)	Netherlands	650	^{18}O	~70	
Crouzet et al. (1970)*	France	570	T		97
		1500	T		99
		9100	T		46

In almost all cases pre-event water accounts for over half (and usually about three-quarters) of the runoff and/or peakflow associated with rainstorms. Except for the Glendhu 2 catchment in New Zealand (McDonnell et al., 1990) and two small catchments near Babinda, Queensland, Australia (see Chapter 11) the similarity of the fraction of pre-event water (f_{pe}) holds true for watersheds of different area, vegetation, and geology. The basins in Table 10.1, located in Europe, North America, Australia, and New Zealand, range over five orders of magnitude in area (0.75 to 7 x 10^4 ha). Most of the watersheds studied were predominantly forested, though at least one was mixed forest and grassland/pasture (Nolan and Hill, 1990) and one all grassland (Bonell et al., 1990). The 3.8 ha M8 catchment in New Zealand was clear-cut, leaving only a 3-10 m wide strip of riparian vegetation, before the studies conducted there (Pearce et al., 1986; Sklash et al., 1986). Most of the sites in Table 10.1 receive annual precipitation of 1000-1300 mm. Permanente Creek (Nolan and Hill, 1990) is the driest, with 400-800 mm/yr (depending on elevation within the watershed), while the wettest sites are Hafron Forest (Neal and Rosier, 1990) and the M8 catchment referred to above, receiving 2400 and 2600 mm/yr, respectively. Sites in Table 10.1 span a wide variety of bedrock types (metamorphics of various grades, intrusive and extrusive igneous rocks, limestone, and clastic sedimentary rocks).

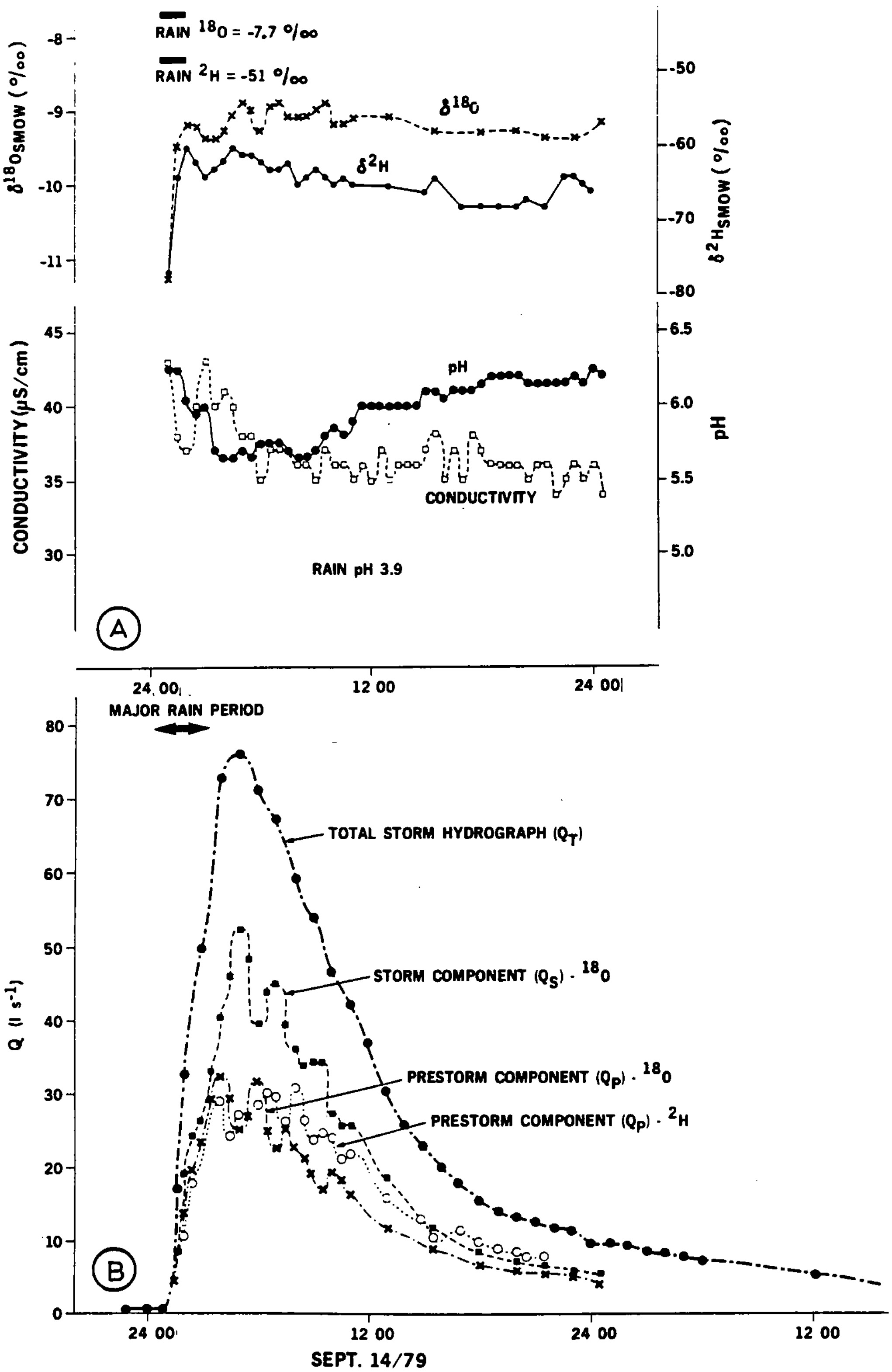

Figure 10.1. Electrical conductivity, pH, δD, and $\delta^{18}O$ data for storm runoff from Harp Lake sub-basin number 4 in Ontario, Canada, and separation of the resultant stream hydrograph into "storm" (event) and "pre-storm" (pre-event) components, for the rainfall event of 14 September 1979 (from Bottomley et al., 1984). The volume-weighted proportion of pre-event water for the hydrograph was about 40%.

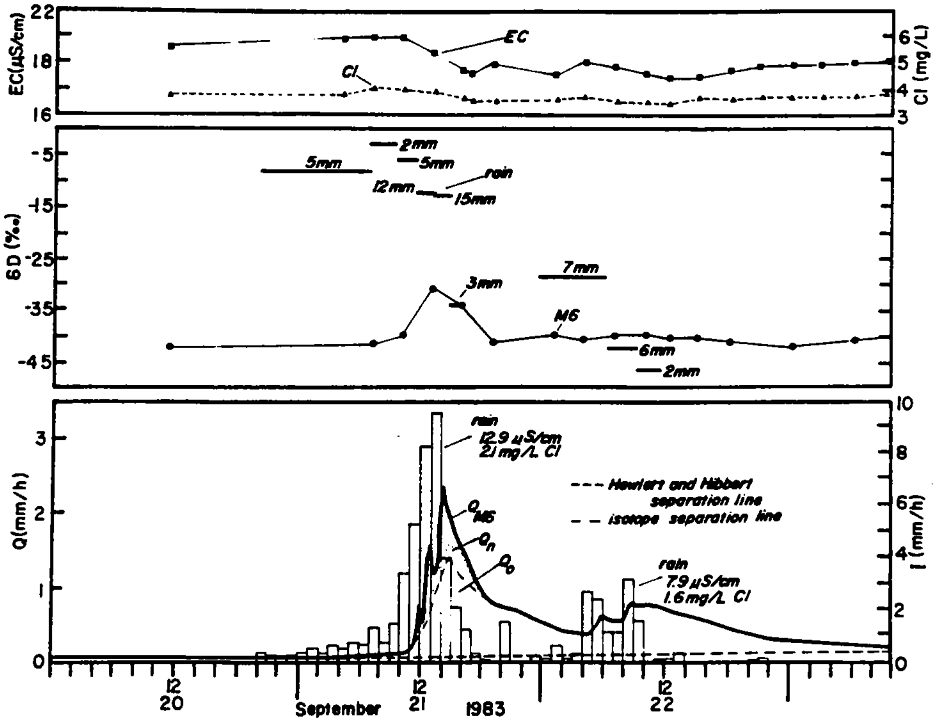

Figure 10.2. Electrical conductivity, chloride, δD, and discharge data for the stream, and δD and rainfall rate data for precipitation, for the M6 catchment at Tawhai State Forest, New Zealand during the rainfall event of 21-22 September 1983 (from Sklash et al., 1986).

The most significant finding of the studies in Table 10.1 is the consistently large fraction of pre-event water in storm streamflow. The discharge of significant amounts of pre-event water to streams during storms is unequivocal proof of the importance of subsurface stormflow in generating stream hydrographs. In this respect, the isotopic studies are in accord with the substantial body of hydrometric studies indicating the importance of subsurface stormflow (e.g., Hursh, 1936; Hursh and Brater, 1941; Hoover and Hursh, 1943; Roessel, 1950; van't Woudt, 1954; Whipkey, 1965, 1969; Weyman, 1970; Troendle and Homeyer, 1971; Harr, 1977; Anderson and Burt, 1978). Nevertheless, many of the subsurface flow studies highlight the importance of rapid throughflow of rain water through soil macropores: the body of isotopic evidence suggests that this is not possible mechanically (see Section 10.2.3). Because Hortonian overland flow would necessarily be composed of new or event water, the isotopic data preclude the dominance of (but not the contribution to) storm runoff by this mechanism at the sites investigated. This is in accordance with other work that has relied on the large difference between rainfall and potential infiltration rates to argue against the widespread occurrence of Hortonian overland flow (e.g., Hewlett and Hibbert, 1967; Freeze, 1972b).

While oxygen and hydrogen isotopic data indicate that subsurface stormflow is important and Hortonian overland flow does not dominate runoff on humid forest and grassland watersheds, one could argue that hydrometric studies had already provided solid support for both of these conclusions by the time the isotopic approach and results started to become widely known (see reference list in previous paragraph). Of course, confidence in the conclusions regarding subsurface stormflow and Hortonian overland flow is enhanced by reaching them independently with both hydrometric and isotopic data, but it is fair to ask whether the isotopic data can offer something more than confirmation of conclusions already well-established through hydrometric investigations. Hydrometric data alone could never reveal the proportions of event and pre-event water in streamflow, but most hydrologists would probably agree that quantitative knowledge of physical runoff mechanisms is the primary goal and isotopes are only useful insofar as they contribute toward this goal. We believe that isotopic data do have something unique and significant to offer beyond the capabilities of hydrometric data: the potential to constrain the hydraulics (mixing and flow) of the subsurface storm response to improve understanding of how infiltration mixes and moves down gradient with pre-event water. We return to this theme later in the chapter.

While the isotopic composition of storm streamflow is sensitive to the type of runoff mechanisms feeding the stream, it is also true that the relative volumes of event and pre-event water influence stream isotopic response. As Pearce et al. (1986) stated, "even a shallow soil profile 1 meter thick will commonly contain 300-500 mm of water at field capacity. It is a reasonable assumption that in any catchment there is some magnitude of runoff event which exceeds the maximum possible storage capacity of the catchment. If events of this size or larger occur, rainfall from the current storm must appear substantially in and eventually dominate the hydrograph." Thus, part of the reason for the large f_{pe} values in Table 10.1 seems to be the small amount of precipitation, relative to the storage of pre-event water, in the events studied.

Examples

One of the best examples of the investigation of stormflow using isotopic and hydrometric methods at a single site is the work done at the M8 catchment in New Zealand. Mosely's (1979) hydrometric work involved monitoring storm response in 8 soil trenches, 1 seep, and two stream channel sites. Dyed water was also injected under wet conditions, and the response monitored at several of the trenches. Rapid subsurface flow in amounts capable of accounting for stream hydrographs was observed at the seep and soil pits. Downslope seepage was observed at the base of the organic soil, above the mineral soil. Also, "where roots, decayed root channels, and other macropores...provide pathways across the interface between the organic and mineral horizons, water moves rapidly into the mineral soil..." (Mosely, 1979). From there it eventually reaches the interface between the mineral soil and the relatively impermeable underlying sediments (compacted Old Man Gravel). This water was found to then move downslope above the Old Man Gravel both as rapid macropore or "pipe" flow and slower seepage through the soil matrix (the latter continuing between storm events).

Sklash et al. (1986) reported on the isotopic and streamflow response of M8 to 3 storms in September 1983. As indicated in Table 10.1, pre-event water accounted for 73-79% of the runoff associated with these events. Sklash et al. (1986) also collected water samples at 6 of Mosely's hillslope sites (5 trenches and the seep). Pre-event water was found to dominate stormflow at all of the sites, accounting for about 60-70% of subsurface stormflow at site A and pits 1, 2, and 3, and > 90% at pit 5 and the seep. The storms studied were of moderate size and duration, having return periods of about 4 to 13 weeks, and occurred over wet, dry, and intermediate conditions. Clearly, the macropore flow observed by Mosely (1979) (and seen "infrequently" by Sklash et al., 1986) was not new (event) water, in contrast to Mosely's assertion in his conclusions. Pearce et al. (1986) and Sklash et al. (1986) discounted Mosely's observations as unimportant to storm runoff and proposed a hypothesis of pre-event storm runoff that relied on the concept of "groundwater ridging", a rapid rise in the water table associated with infiltration in the riparian zone. However, while the isotopic data showed that

Mosely's use of the phrase "new water" had been an inappropriate description of the macropore flow on M8, it did not otherwise discredit Mosely's observations of macropore flow. Clearly the stage was set for development of a theory of pre-event water flow in macropores.

McDonnell (1990) built on the work of Mosely (1979), Pearce et al. (1986), Sklash et al. (1986) and others to provide a plausible explanation for the contribution of pre-event water to stormflow via macropore flow. McDonnell used nests of continuously recording tensiometers to observe the response of soil moisture during storms. Data indicated that water perched above the interface between organic soil and mineral soil (as reported previously by Mosely) and moved quickly as "bypass flow" (bypassing the soil matrix) to the base of the mineral soil along preferential flowpaths (vertical cracks). There, above the top of the Old Man Gravel, the infiltrated water filled the small amount of available air-filled pores (usually less than 10% of the total porosity, as reported previously by Mosely), creating a saturated zone at the base of the mineral soil. This saturated zone was then drained by rapid macropore or pipe flow in the lower mineral soil. Because the saturated zones thus created would consist of 90% or more pre-event water (the percentage of total porosity occupied by water at the start of the storm), the downslope macropore flow would be mostly pre-event water, in accordance with isotope data from Pearce et al. (1986) and Sklash et al. (1986). In the case of the M8 catchment, McDonnell's synthesis of the hydrometric and isotopic data reveals how event and pre-event waters may mix in the subsurface and how the latter may be displaced from the soil matrix into macropores where it may move rapidly through the subsurface to contribute to stream hydrographs. Taken alone, neither type of data (hydrometric or isotopic) could have advanced the understanding of storm runoff on M8 as much as the combination of the two together.

In addition to the analysis of pre-event water flow in macropores, McDonnell (1990) also documented the response of the near-stream zone during storms, in particular the rapid increase of pressure heads at the beginning of storms and the much slower decrease following cessation of rainfall. The quick response of the water table was attributed to the high soil moisture (i.e., low available storage) of riparian soils on the M8 catchment. While the near-stream response was rapid, order-of-magnitude calculations with Darcy's equation showed that this response was not sufficient to explain the peak discharge of pre-event water to the stream during many storms (including those studied by Sklash et al. (1986)). Storm runoff of pre-event water was dominated by seepage and macropore discharge from small hollows adjacent to deeply-incised, ephemeral first-order streams feeding the main perennial channel, rather than by displacement of riparian groundwater.

Rapid increases in riparian groundwater levels (so-called groundwater "mounding" or "ridging") have often been invoked to explain the increased fluxes of pre-event water that are observed during storms (Sklash and Farvolden, 1979; Sklash et al., 1986; Blowes and Gillham, 1988). The assumption is that the combination of increased hydraulic gradient and larger saturated cross-sectional area adjacent to the stream channel is adequate to account for increased discharge of pre-event water to the stream. The focus on the near-stream area may seem reasonable, given the fact that pre-event water flow has in some cases been observed to peak before event water or total stream flow (e.g., Bonell et al., 1990; Waddington et al., 1993). Most authors invoking the rapid groundwater mounding mechanism explain its occurrence by reference to the conversion of a capillary fringe to positive (greater than atmospheric) pressure upon infiltration of event water. While laboratory studies (e.g., Abdul and Gillham, 1984) show this phenomenon to be possible in principle, we know of no evidence that it has or does actually occur in any field setting. McDonnell (1990) notes that:

> In the soil physics literature...the notion of a soil having a tension-saturated zone, or capillary fringe, has been questioned. Field retention data have failed to observe significant zones of tension saturation in clays and loams (Perroux et al., 1982), and Clothier and Wooding (1983) even question the presence of such zones in laboratory media.

However, the groundwater ridging mechanism need not rely on the existence of a capillary fringe. It requires only that available storage (air-filled porosity) in the vadose zone be low, through some combination of proximity of the top of the saturated zone to the ground surface (which may be affected by a capillary fringe) and/or high soil moisture.

Even when there is a significant response of the near-stream water table to infiltration, that response may still be insufficient to explain storm discharge of pre-event water to the stream (e.g., McDonnell, 1990). In at least one case, increases in groundwater head were contemporaneous with decreases in head gradient toward the stream. While Sklash and Farvolden (1979) found that "very large and rapid increases in the hydraulic head in the near-stream groundwater occur soon after the onset of rain", they also noted "that the near-stream hydraulic gradient may decrease slightly from its pre-storm value." From the standpoint of water fluxes to the stream, the observation concerning gradient is clearly the more salient one.

In a manner similar to McDonnell (1990), Waddington et al. (1993) argued that the near-stream water table response at their site in Ontario was too small to account for storm fluxes of pre-event water to the study stream. Based on observations at one soil pipe, Waddington et al. (1993) concluded that discharge from soil pipes at the bases of hillslopes was a significant source of pre-event water to the study stream during storms, but that this flow responds too slowly to account for the large f_{pe} at peak flow. Their explanation for the large fraction of pre-event water in storm streamflow (87% and 93% at peak flow for the two streamflow hydrograph separations reported) was based on their "rapid surface water mixing" hypothesis. Evidence for the hypothesis comes largely from work on a 190 m^2 wetland plot about 40 m from the stream channel. About one-third of the plot (60 m^2) was a groundwater discharge area covered with an average depth of 13 mm of water. It was found that "piezometric heads (on the wetland plot) remained virtually unchanged during and after storm events of varying intensity and duration" (Waddington et al., 1993). Storm runoff from the plot seemed to be dominated by saturation overland flow consisting of a mixture of event and pre-event water, with the mixing proportions determined by the rate of throughfall on the saturated ground surface (4.5 to 11.3 mm/hr) and the (nearly steady) rate of groundwater discharge to the ground surface (6 to 18 mm/hr at baseflow).

Waddington et al. (1993) also write that:

> ...peak (overland) flow from the saturated area was dominated by pre-event water (more than 77%). Hydrograph separation of the basin outlet storm discharge showed peak flow pre-event water fractions of over 87-93%, which is consistent with the saturated area response *and indicates that the same process is operating at the basin scale.* (Italics are ours.)

While the conclusions regarding runoff processes on the saturated wetland plot are probably correct, one must be skeptical of the extrapolation of these processes to the entire 160 ha watershed based solely on the similarity of f_{pe} values at the plot and watershed scales. For example, we have already discussed how Sklash et al. (1986) and Pearce et al. (1986) found f_{pe} values of 73-97% at a site in New Zealand dominated by subsurface runoff, as more recently described by McDonnell (1990). Waddington et al. (1993) found values within this range (77-93%) for saturation overland flow on their wetland plot, illustrating a critical point mentioned earlier: there is not a unique relationship between runoff mechanisms and the fraction of pre-event water in runoff. Furthermore, Buttle (1994) discussed in detail how different mechanisms may lead to similar f_{pe} values. Saturation overland flow may be an important runoff mechanism basin-wide at the study site of Waddington et al. (1993), but this is not necessarily indicated (and is not proved) by the similarity of f_{pe} values at plot and basin scales.

The results of Blowes and Gillham (1988) provide an interesting contrast to those of Waddington et al. (1993), in the sense that near-stream water table response was much larger yet the fraction of pre-event water in the stream hydrograph was much smaller for the former study. For example, for one May storm involving 8.8 mm of precipitation over a 12 hour period, Blowes and Gillham (1988) used ^{18}O data to show that 50% of the hydrograph volume was due to pre-event water (called "groundwater" by the authors). Water table elevation rose 19 cm during this storm. Waddington et al. (1993) found negligible water table response for storms resulting in hydrographs with 87% and 93% pre-event water. The contrast underscores the point that there is not a unique relationship across study sites between the magnitude of water table response and the fraction of pre-event water in the associated hydrograph. Relationships between f_{pe} values and flowpaths will generally vary from site to site, and should in general be worked out in the field with the combined use of hydrometric and isotopic measurements.

A particularly vivid example of the lack of correspondence between f_{pe} and run-off mechanism is provided by Kendall (1993) reporting on a storm event at the artificially constructed Hydrohill catchment at the Chuzhou Hydrology Laboratory located in northeastern China near Nanjing. After a hillslope was excavated to bedrock, a concrete aquiclude consisting of two intersecting slopes dipping towards each other at a 10-degree angle was constructed with an overall downslope gradient of 14 degrees. Sidewalls were constructed of concrete to prevent any lateral infiltration from the surrounding bare rock areas to define a 490 m^2 catchment. The area was filled with a silty loam to a depth of approximately 1 m. During infilling the bulk density of the soil was maintained to approximate the natural soil profile; grass was planted over the entire basin. The soil was allowed to settle for 3 years. After this time, a drainage trough was dug at the intersection of the two slopes. Five fiberglass troughs, each 40 cm wide and 40 m long, were installed longitudinally in the trench, staked on top of one another to create a set of long zero-tension lysimeters that isolated five different flowpaths: rain, surface run-off, the 0 to 30 cm soil layer, the 30 to 60 cm soil layer and the 60-100 cm soil layer. This facility presents a unique opportunity to directly observe separate flowpaths.

During the rainstorm reported by Kendall (1993), the groundwater levels never reached above the soil surface, so two physically distinct flowpaths can be unambiguously defined: surface runoff and subsurface runoff. Table 10.2 contains the proportion of new water contained in these two physically defined flowpaths as calculated by isotopic and two commonly used chemical tracers, Cl and SiO_2. The surface runoff was entirely event water, consistent with physical observations. However the overall proportion of event water (88%) did not correspond with the physical flowpath proportions (62% subsurface runoff, 38% surface runoff). Kendall (1993) was able to close a mass balance for ^{18}O in this storm using well and soil moisture data. From these calculations, she found that subsurface runoff contained more event water than expected. She suggested that rain followed preferential flowpaths to the troughs during the event and that the entire catchment did not respond uniformly to the input.

Table 10.2. Comparison of Chemical and Isotopic Hydrograph Separations at Hydrohill (modified from Kendall, 1993).

Physically Measured Flow	Percent of Total Flow	Percent Event Water Calculated With:		
		SiO_2	Cl	^{18}O
Surface	38	65	80	100
Subsurface	62	32	39	84
Total	100	36	45	88

If one had sampled only the outlet of the catchment, it would appear that the chemical tracers did capture the physical flowpaths: the proportions of new water calculated from these tracers (36 and 45%) tightly bracket the observed proportion from the surface trough. The values from the individual troughs, however, indicate that this is a fortuitous occurrence: the tracers are highly non-conservative, with both silica and chloride being rapidly dissolved in the event water, as indicated by fact that the surface-runoff component did not contain 100% new water. Even in this highly controlled artificial catchment, there is a high degree of heterogeneity in water movement through the porous medium. Determining the proportion of event water alone does not constrain the possible hydrologic mechanisms sufficiently to uniquely distinguish subsurface and surface flowpaths through the catchment.

10.2.4 Scale dependence of f_{pe} values

While spatial scale is widely recognized as one of the most important parameters in hydrologic studies, there are at present very few data on the variability of f_{pe} within a single watershed over the range of scales most relevant to watershed modeling. The data of one of the earliest studies (Sklash et al., 1976) come closest to fitting this description. Measurements were made at seven different points in two adjacent watersheds; the largest number of points on any individual branch of a drainage system was three. Watershed areas upstream of these three points were roughly 100, 400, and 700 km^2 (see Table 10.1), and f_{pe} values were 55, 71, and 70 percent, respectively (at the Otterville, Tillsonburg, and Vienna sites, respectively, in Figure 10.3), for the one storm reported. Mook et al. (1974) measured ^{18}O concentrations at three points in the stream draining their study site; the three points defined watersheds of roughly 0.25, 1.5, and 6.5 km^2 (estimated from their map). Data were reported only for the site farthest downstream, though it was stated that data from the other two sites were similar. Pearce (1990) found similar

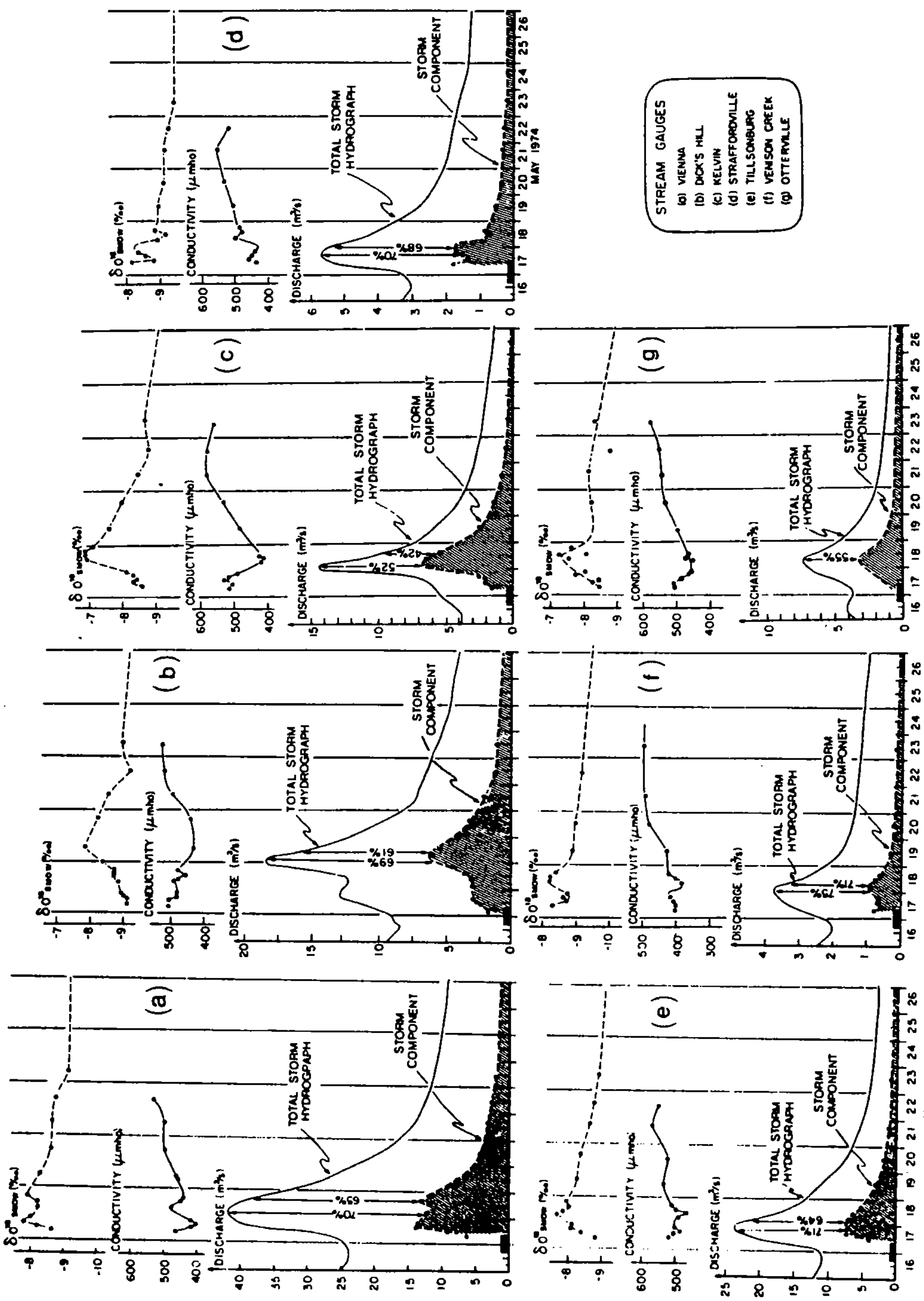

Figure 10.3. Electrical conductivity and $\delta^{18}O$ data, and event/pre-event hydrograph separations, from seven different sites in the Big Creek and Big Otter Creek watersheds in Ontario, Canada, for the rainfall event of 16 May 1974 (from Sklash et al., 1976).

f_{pe} values decreased with catchment size for the 0.038 km^2 M8 catchment (discussed earlier) and a 0.003 km^2 subcatchment within it, though the larger 2.8 km^2 catchment containing M8 showed smaller f_{pe} values at peak flow. This behavior is opposite to that shown by Sklash et al. (1976), where the smallest watershed had the smallest f_{pe}. Two studies (Sklash et al., 1986; Waddington et al., 1993) report measurements at plots or soil pits within a watershed, in addition to measurements made at the watershed outlet. The few available data do not provide a clear picture of the dependence of f_{pe} values on spatial scale, making this an issue to be resolved by ongoing and future work. New work suggests that results continue to be equivocal. Brown et al. (1998) reports that for 7 nested catchments (5 - 200 ha) in the Catskill Mountains of New York, that new water decreases with catchment size. McDonnell et al. (1998) report for 4 nested catchments in New Zealand (ranging in size from 0.05 - 1000 ha) that new water *increases* with catchment size.

10.2.5 Intra-component variability in tracer concentrations

Implications for uncertainty in calculated pre-event water fractions

As stated in Section 10.2.2, ^{18}O, D, and T may be used in a two-component mixing model if the isotopic difference between event and pre-event water is large relative to the intra-component variability of each and the measurement uncertainty associated with the isotopic analyses. The mixing equation used to determine f_{pe} for a stream or other water sample is:

$$f_{pe} = \frac{C_s - C_e}{C_{pe} - C_e} \tag{10.1}$$

where C_{pe}, C_e, and C_s are the concentrations of the isotopic tracer in pre-event, event, and sample water, respectively. Either δ values in parts per thousand (‰, per mil) or isotope ratios such as $^{18}O/^{16}O$ can be used as "concentrations" in Equation 10.1. The uncertainty in f_{pe} (W_{fpe}) can be expressed in terms of the uncertainties in the tracer concentrations (Genereux, 1998):

$$W_{fpe} = \sqrt{\left[\frac{C_e - C_s}{(C_{pe} - C_e)^2} W_{cpe}\right]^2 + \left[\frac{C_s - C_{pe}}{(C_{pe} - C_e)^2} W_{ce}\right]^2 + \left[\frac{1}{(C_{pe} - C_e)} W_{cs}\right]^2} \tag{10.2}$$

where W_x corresponds to the uncertainty in x. From inspection of Equation 10.2 it is apparent why a large difference between the isotopic composition of event and pre-event waters is beneficial; the larger C_{pe} - C_e, the smaller W_{fpe}. Also, it can be seen that the uncertainty in f_{pe} is most sensitive to uncertainty in C_s, since the multipliers on W_{cpe} and W_{ce} differ from the multiplier on W_{cs} by factors of $(C_e-C_s)/(C_{pe}-C_e)$ and $(C_s-C_{pe})/(C_{pe}-C_e)$, respectively, ratios whose absolute magnitudes are always less than one for mixtures of event and pre-event water. This is fortunate because C_s is generally the tracer concentration with the smallest uncertainty (typically just the analytical uncertainty of the isotope measurement). Inspection of the error terms for C_{pe} and C_e shows that W_{fpe} is more sensitive to error in the component (event or pre-event water) accounting for more than half of the mixture (pre-event water in most cases).

Table 10.3 shows the results of some example calculations with Equation 10.2 for a hypothetical case in which precipitation of $\delta^{18}O$ = -6‰ falls on a watershed where pre-event water has $\delta^{18}O$ = -12‰, and a stream sample with $\delta^{18}O$ = -10‰ is collected. The stream sample would of course have f_{pe} = 0.67; the last column in Table 10.3 gives the uncertainty in this f_{pe} value, given different values for the uncertainty in C_{pe} (-12‰) and C_e (-6‰). The uncertainty in C_s is taken to be ±0.1, the approximate value of the analytical uncertainty in $\delta^{18}O$ measurements. Results show that f_{pe} is more sensitive to error in C_{pe} than error in C_e (because pre-event water accounts for more of the stream sample than event water), but significant amounts of uncertainty in either C_{pe} or C_e (around ±1‰ or more) introduce sizable error in calculated f_{pe} values. Thus natural intra-component variability of this magnitude is of concern for isotopic hydrograph separations and resultant conclusions regarding runoff mechanisms. Genereux (1998) presents a detailed analysis of tracer-based uncertainty for those readers seeking additional detail on the topic.

Table 10.3. Uncertainty in f_{pe} calculated using selected values of W_{cpe} and W_{ce} in Equation 10.2. The value of W_{cs} is taken to be ±0.1. See text for discussion.

W_{cpe} (error in C_{pe})	W_{ce} (error in C_e)	W_{fpe} (error in f_{pe})
0.1	0.1	0.021
0.2	0.1	0.028
0.3	0.1	0.038
0.5	0.1	0.058
1.0	0.1	0.112
2.0	0.1	0.223
0.1	0.2	0.023
0.1	0.3	0.026
0.1	0.5	0.034
0.1	1.0	0.059
0.1	2.0	0.113
0.2	0.2	0.030
0.3	0.3	0.041
0.5	0.5	0.064
1.0	1.0	0.125
2.0	2.0	0.249

Variability in pre-event water

Several examples from the literature document spatial variability in the isotopic composition of pre-event water (while the isotopic composition of pre-event water may vary in time from season to season, only spatial variability at a given time is relevant to isotopic hydrograph separation during and following a particular storm). Blowes and Gillham (1988) found that the $\delta^{18}O$ of pre-event water varied between -5.3‰ at about 10 cm below ground surface to -9.5‰ at 3 m below ground surface in May, 1982. Blowes and Gillham (1988), like other authors, chose the $\delta^{18}O$ of pre-storm streamflow (-7.9‰ for May 1982 storms) as the best $\delta^{18}O$ value to use for pre-event water in hydrograph separations. The $\delta^{18}O$ of baseflow represents an integrated average $\delta^{18}O$ for the pre-event water actually arriving at the stream, and as such may represent the best practical choice for isotopically defining pre-event water. However, if flowpaths change during a storm, the flow-weighted average $\delta^{18}O$ of pre-event water discharging to the stream may also change, introducing error into hydrograph separations which assume the isotopic signature of pre-event water reaching the stream during the storm is unchanged from that of baseflow.

Sklash and Farvolden (1979) found $\delta^{18}O$ values of about -11.9‰ in jointed gneiss bedrock at their study site in Quebec (Ruisseau des Eaux Volées), while groundwater in the overlying glacial deposits had $\delta^{18}O$ values around -12.8‰. Probably even more significant with respect to hydrograph analysis was the fact that "^{18}O analyses of the vadose water indicate ... values are consistently heavier than the groundwater by as much as 6 ppt" (Sklash and Farvolden, 1979). Because this large isotopic variability in pre-event water could lead to a substantial uncertainty in hydrograph separation, Sklash and Farvolden (1979) sought to undertake separations only for those hydrographs without a significant contribution from vadose zone water. However, the graphical procedure applied to detect such hydrographs was faulty in that it could lead to both "false positives" (incorrectly identifying a hydrograph as having a significant contribution from vadose zone water) and "false negatives" (failing to identify hydrographs with a significant contribution from vadose zone water). The procedure (Sklash and Farvolden, 1979) relied on plots of $\delta^{18}O$ vs. streamflow rate (Q). It was assumed that mixtures of groundwater and precipitation would fall along a straight line connecting baseflow and peakflow on such a plot; further, it was assumed that contributions from isotopically-heavy vadose zone water would cause data to plot above this straight line. However, both of these assumptions may be violated. Stream samples composed of water from three distinct components (groundwater, vadose zone water, and precipitation) could potentially fall along a straight line on a plot of $\delta^{18}O$ vs. Q. In addition, time-varying samples of a two-component mixture (groundwater and precipitation) will not necessarily fall along a straight line on the $\delta^{18}O$ vs. Q plot. Hysteresis in flowpaths between the rising and falling limbs of a hydrograph could produce different isotopic signatures for the mixture (streamwater) at the same Q. This phenomenon is well known for the storm response of chemical solutes; in addition, it is apparent in more recent isotope data (published after Sklash and Farvolden's paper) showing that the peak in event water discharge sometimes follows the peak in total hydrograph discharge (Bonell et al., 1990; Waddington et al., 1993). This phenomenon could also explain some of the results of Sklash and Farvolden (1979).

Turner et al. (1987) found smaller differences between vadose zone water and groundwater. The ^{18}O content of "deep" groundwater was found to be highly uniform and equal to 5.0‰ ("deep" was not defined, but appears from the text and Figure 2 of the paper to be greater than several and less than about 25 meters below ground surface), while "shallow" groundwater was slightly more variable and heavier on average (-4.1‰). Vadose zone water was said to have been highly uniform and "depleted by about 0.4 ppt in $\delta^{18}O$ ... relative to the deep groundwater samples" (Turner et al., 1987). Neal et al. (1992) used isotopic data for rainfall and streamflow to indirectly demonstrate variability in the isotopic composition of pre-event water at their site. During two of three storms studied, the isotopic composition of streamwater shifted away from that of precipitation, indicating there were contributions to storm streamflow from pre-event water with an isotopic composition distinct from that of pre-event baseflow. Any simple mixing model for storm runoff would require at least three components on such a basin.

DeWalle et al. (1988) used a three-component model to account for variability in pre-event water on the Fish Run catchment in Pennsylvania. Soil moisture in the vadose zone was found to be 2-3‰ heavier than stream baseflow prior to two events in November 1986. Precipitation associated with these storms resulted in the isotopic composition of streamwater shifting away from that of throughfall and toward that of soil water at some sampling times. As the authors noted, the standard two-component mixing model can not be applied to such situations. The three-component model separated storm streamflow into groundwater, soil water, and channel precipitation (a "geographic source" separation, in the terminology of Sklash et al. (1979)). A three-component model requires one additional constraint (a second tracer or a physical measurement of the flow from one component) beyond what is needed for a two-component model. DeWalle et al. (1988) supplied this extra constraint by calculating the rate of channel precipitation as the product of the throughfall rate and the surface area of the stream. The surface area of the stream was based on a regression equation of stream surface area versus streamflow rate, determined by surveying the stream surface area at four different streamflow rates and fitting a curve to the four points. Results from six storms showed that channel throughfall accounted for 0-14% of storm streamwater, groundwater was 69-100%, and soil water accounted for 0-40%. This work documents the significance of shallow soil water stormflow during precipitation events. In fact, the soil water fluxes are probably underestimated because of the way in which the groundwater component was defined. As pointed out by Genereux and Hemond (1990b):

> In their analysis of storm runoff, DeWalle et al. ... defined the groundwater component to be isotopically equivalent to the pre-storm streamwater... Using this definition with the 3C (three-component) model of DeWalle et al. requires the assumption that soil water does not contribute to baseflow. Results from several hydrometric studies have concluded that unsaturated lateral flow is important in baseflow maintenance (e.g., Hewlett and Hibbert, 1963; Weyman, 1970, 1973; Mosely, 1979)... Unless there are valid reasons to exclude the soil water contribution to baseflow on Fish Run, the ground water $\delta^{18}O$ used by DeWalle et al. will be biased toward that of soil water, and the net effect on stormflow analysis will be to underestimate the true soil water contribution.

Variability in event water

In principle either spatial or temporal variability in the isotopic composition of event water could pose a problem for isotopic hydrograph separation. There are well-known large-scale variations of the isotopic composition of precipitation with latitude and elevation (see Chapter 3 of this volume). These spatial trends could be significant in isotopic analysis of runoff in large basins, though intra-storm temporal variability is probably more troublesome to traditional hydrograph separation studies on small watersheds. Pionke and DeWalle (1992) documented intra-storm variability in the ^{18}O content of precipitation during ten storms at a site in Pennsylvania. Summary data (Table 10.4) show very large ranges in $\delta^{18}O$ for some storms, particularly the larger, longer storms. As shown earlier, variability of this magnitude can have a significant effect on the uncertainty in a calculated f_{pe} value. Pionke and DeWalle (1992) found that the ^{18}O content of precipitation changed most rapidly during periods of high rainfall rate, the same effect observed by Matsuo and Friedman (1967) for at least some of their monitored storms (their storm 3, in their Figure 1a).

Table 10.4. Total rainfall depth, duration, and range and mean of $\delta^{18}O$ for ten storms, from Table 1 of Pionke and DeWalle (1992).

Depth (mm)	Duration (hr)	$\delta^{18}O$ (‰)		
		mean	maximum	minimum
3.8	0.7	-10.00	-9.94	-10.43
9.9	0.5	-9.91	-9.60	-10.90
10.2	0.7	-4.04	-3.71	-4.60
10.6	1.1	-3.51	-3.48	-3.57
17.5	9.0	-3.97	-2.34	-5.78
18.5	4.8	-7.40	-3.86	-9.63
31.0	11.0	-15.41	-4.00	-19.97
31.7	3.0	-8.48	-7.21	-12.42
48.2	9.7	-9.33	-2.53	-12.11
58.2	1.8	-4.89	-2.70	-5.91

McDonnell et al. (1990) studied the effect of intra-storm isotopic variability in precipitation on separation of a hydrograph from the Glendhu 2 catchment in New Zealand. δD of the precipitation became heavier during the storm, from -94.8‰ at the start to -61.9‰ at the end about ten hours later. Three different hydrograph separations were performed (Figure 10.4), each using a different method to determine the δD value of event water (i.e., C_e) for use in Equation 10.1:

1. *Standard weighting*: the depth-weighted average δD of the precipitation was calculated and used as C_e at every time during the storm (this is the approach traditionally used).
2. *Incremental mean*: C_e at a particular time was determined as depth-weighted mean δD up to that time. In this way precipitation not yet fallen does not affect the hydrograph separation.
3. *Incremental intensity*: similar to incremental mean, except that δD values were weighted by average rainfall rate over an interval rather than total rainfall amount over the interval.

Results showed that the standard weighting procedure significantly underestimated the contribution of pre-event water, relative to the other two techniques, during the rising limb of the hydrograph. The f_{pe} determined by standard weighting started off about 30% lower than the values derived from the two incremental methods (which gave very similar results throughout), and eventually merged with the results from the incremental methods around or shortly after peak flow. In the absence of detailed information on the travel time of new water through a catchment, the two incremental approaches are presently the best approach to handling the temporal variability in the isotopic composition of precipitation (at least they improve on the simple standard weighting approach by not allowing C_e at a given time to be affected by precipitation falling after that time).

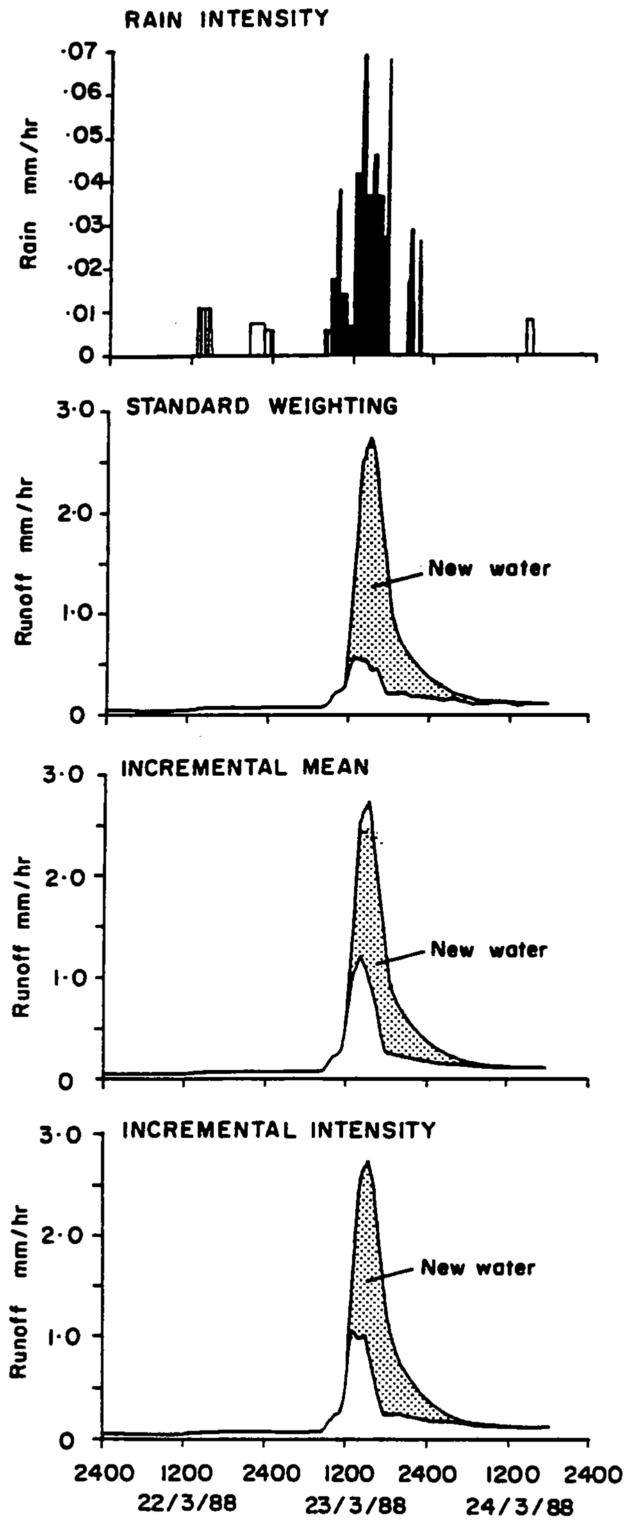

Figure 10.4. Rainfall rate and three different hydrograph separations (based on the same δD data) for the 23 February 1988 storm at the Glendhu 2 watershed in New Zealand (from McDonnell et al., 1990). The three separations are based on different methods for handling the temporal variability in the δD of rainfall (see text for discussion).

10.2.6 Recommendations for field studies

Perhaps the most important and general recommendation that can be made regarding hydrograph separation studies with oxygen and hydrogen isotopes is to respect the limitations of the approach. This begins with an appreciation for the basic logic of the separation (that one is distinguishing water falling as precipitation during a particular storm from water stored on the watershed before the start of the storm), and is reinforced through use of language that is strictly consistent with this logic (e.g., "old" vs. "new" water, or "pre-event" vs. "event" water, as distinguished from other hydrologic terms such as groundwater and overland flow (Sklash et al., 1976)). While it is true, as argued earlier, that much of the impetus for "time source" separation of event and pre-event water is to constrain other separations of more fundamental hydrologic significance ("geographic source" and/or "runoff mechanism" separations), realization of that goal will, in practice, usually require additional measurements beyond oxygen and hydrogen isotopes. Thus, combination of hydrometric measurements (of water flow, head, or storage) with isotopic measurements is strongly recommended. The work done in New Zealand and summarized earlier demonstrates the value of this approach; the work of Waddington et al. (1993) provides another good recent example.

Recent studies demonstrate the significant isotopic variability within both event and pre-event water. Because this variability may control the uncertainty in the hydrograph separation, it is of prime importance to have some data with which to evaluate it. In general this calls for sequential sampling of rainfall (or more specifically, throughfall; see below) to evaluate the temporal variability of event water composition, and spatially distributed sampling of pre-event water in the subsurface. As Pearce et al. (1986) point out, evaporation from intercepted water on a forest canopy could result in throughfall being enriched in the heavier isotopes of oxygen and hydrogen relative to precipitation. Spatial variability in the isotopic composition of pre-event water has been evaluated in several studies, and found to be significant. Some authors have taken the isotopic composition of pre-event streamflow as representative of pre-event water, on the supposition that even if there is a heterogeneous distribution of pre-event isotopic composition in the subsurface, streamflow generation processes operate to provide the true flow-weighted average composition of water reaching the stream, the composition that is of interest from the standpoint of the hydrograph separation. The major concern with this approach is that subsurface flowpaths likely change during the storm, and if these changes affect the flow-weighted average isotopic composition of pre-event water reaching the stream (e.g., isotopically heavier water from higher in the soil profile becomes relatively more important) they will introduce error into the hydrograph separation. Efforts should be made to <u>minimize</u> (by working under conditions when pre-event water is relatively homogeneous, and there is a large difference in event and pre-event composition) and <u>quantify</u> (through spatial sampling of pre-event water to determine its variability, and quantitative propagation of this variability to estimate uncertainty in f_{pe}) this error in hydrograph separation. Ideally, at least several subsurface sampling sites would be used, with a greater site density toward the lower slopes and riparian areas which water must traverse *en route* to the stream. A formal geostatistical approach to quantification and modeling of pre-event water variability has not been attempted, but it would be a useful addition to understanding the structure of this variability.

10.3 New Directions

10.3.1 Subsurface mixing and residence time

Some authors have sought out frameworks other than separation of event and pre-event water for use of oxygen and hydrogen isotope data in streamflow generation studies. Several studies have applied stable isotope data to the determination of water residence times or apparent streamflow "ages" on catchments. Most of the work on water residence times involves deconvoluting the time course of isotope input (i.e., the isotopic composition of precipitation or throughfall) with a system response function (also called weighting function) to calculate the time course of isotope output (i.e., the isotopic composition of streamwater) from the catchment. Adjusting the response function to optimize the fit between measured and computed streamwater isotope content gives a mean residence time for water (τ) and possibly, depending on the form of the response function used, an additional "dispersion" parameter (see below). τ and, if applicable, the dispersion parameter, can be used in the response function to calculate the distribution of water residence times. Chapter 21 reviews these techniques in some detail.

Rose (1993, 1996) adopted a somewhat different approach in his use of tritium to constrain water residence times on four catchments in Georgia. Rose (1993) found the mean T content of baseflow to be about 20-30 tritium units (TU) on three catchments of the Upper Ocmulgee basin. This information was used to constrain the mean residence time of water providing baseflow as follows:

- It was assumed that water discharged as baseflow had a normal distribution of residence times.
- A mean τ and standard deviation S_τ were chosen for this normal distribution (τ values chosen ranged between 10 and 45 years, S_τ values ranged from 1 to 15 years).
- The area under the normal distribution with the chosen τ and S_τ values was taken to be 1, and was divided up into time intervals to give weighting fractions for the contribution of water from each time interval (since 1953) to the baseflow in 1991 (the year of data collection). (It was somewhat unclear from the original paper whether the time intervals were 1 or 2 years).
- The weighting fraction for each time interval was multiplied by the decay-corrected T content of rainfall during that interval (i.e., the T content water from that rainfall would have had in 1991) to give the fractional contribution of T from that time interval to the 1991 baseflow.
- The fractional contributions were added to give the model-computed T content of 1991 baseflow, which was then compared to the true T content of 1991 baseflow to evaluate how realistic the chosen τ and S_τ values were.

This procedure was applied to combinations of τ values between 10 and 45 years and S_τ values between 1 and 15 years, yielding agreement between true and model-computed T values in baseflow for τ values between 15 and 30 years. Rose (1993) suggested that these residence times are consistent with expected rates of vertical downward flow through saturated regolith, though a specific argument was not offered for why τ would be controlled by rates of vertical rather than horizontal flow. Rose (1996) carried out a similar procedure to constrain the range of possible residence time values for groundwater sampled near a ridge on Falling Creek basin (187 km^2) in Georgia. Residence times from 5 to 100 years were investigated using the computational procedure outlined above, and those in the range 20 - 40 years gave good agreement between measured and model-computed T content.

Harris et al. (1995) proposed a new hydrograph method for source area modeling based on continuous open system isotopic mixing using a variable source area and three isotopic reservoirs. These three reservoirs were 1) direct precipitation onto saturated areas, 2) a near-stream saturated zone, and 3) subsurface water in upslope areas (Figure 10.5). They allowed the reservoir sizes and isotopic compositions to evolve due to continuous, open system mixing. They found that streamflow was composed of rainfall on saturated areas and water exfiltrated in the near-stream zone. The contributing source fractions were determined using the observed isotopic compositions of the stream and the modeled isotopic compositions of the contributing reservoirs, which were functions of time. The near-stream saturated zone received inflow from the upslope areas which were not surface saturated (Figure 10.5). The surface saturated area was allowed to change dynamically based on the difference between lateral inflow and contributions to streamflow from the near-stream saturated zone. The upslope zone (reservoir 3) evolved by mixing with rainfall. The Harris et al. (1995) hydrograph separation model required 1) a function which relates the amount of water stored in the near-stream saturated zone to saturated area, 2) a function which relates saturated area fraction to total streamflow (similar to that used by DeWalle et al. (1988) as discussed in Section 10.2.5), and 3) knowledge of the water storage capacity in reservoirs 2 and 3.

The hydrograph separation method was applied by Harris et al. (1995) to oxygen isotope data for rainfall and runoff during a 36-hour storm at the Gårdsjön F1 catchment in southwestern Sweden (described in Chapter 12). This method was used to estimate parameters for relations between saturated area fraction and streamflow, and saturated area and subsurface water storage. Harris et al. (1995) showed that streamflow contributions from overland flow could be described by a simple analytic function of antecedent conditions and catchment processes. This approach is of interest as many new studies highlight the importance of the riparian zone on imparting the chemical signal of streamwater (Hooper et al., 1998). The mixing of distinct reservoirs is now being attempted in several current projects.

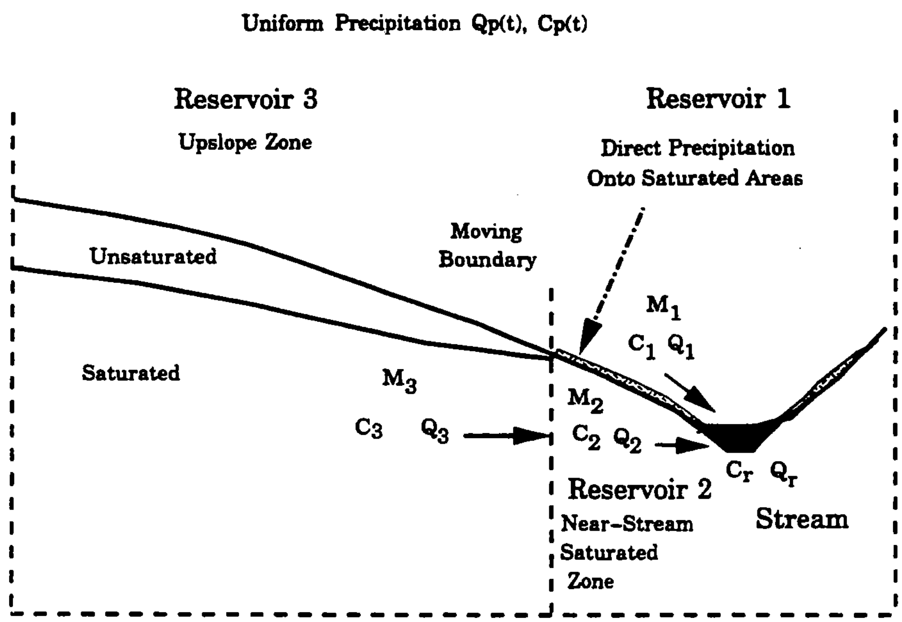

Figure 10.5. Schematic diagram of continuous open system isotope mixing model (From Harris et al., 1995). Arrows indicate model flux directions; dashed line indicates boundary limiting surface-saturated areas of catchment; hachured area is surface saturated; and solid area represents the stream.

10.3.2 Use of isotopes in model calibration

In addition to their application in hydrograph separation and residence time studies, oxygen and hydrogen isotopes have been used in the calibration of catchment rainfall/runoff models, particularly "conceptual" hydrochemical models. These are lumped-parameter models where the catchment is divided into compartments that represent different conceptual units, such as soil horizons, which are thought to influence streamwater chemistry. Predictions of streamwater chemistry are more sensitive to the routing of water through these internal compartments than are predictions of the quantity and timing of streamflow. The main impetus for this research was the prediction of the effects of acid deposition on streamwater chemistry, but the problem is generic to determining the effects of any non-point source pollutant on surface waters.

In this application, only the conservative behavior of the isotopes is assumed; that is, the isotopes move as the water moves and do not fractionate between the time the water reaches the ground and the time the water exits the catchment as streamflow. This assumption is generally supported for catchments with little surface water (Dinçer and Davis, 1984; Sklash and Farvolden, 1979). None of the other assumptions for hydrograph separation, as outlined above, are needed. The isotopic tracer is being used to provide more insight into the movement of water through the catchment, and to provide additional information for model calibration. The central issue is "parameter identifiability"; that is, do the data that are available define a unique parameter set for the model or are multiple parameter combinations able to reproduce the data equally well? Model predictions become increasingly uncertain as the range of acceptable parameter values widens.

The Birkenes model (Christophersen and Wright, 1981; Christophersen et al., 1982) has been most extensively evaluated using isotopic tracers. It represents the catchment as two linear reservoirs. For the snow-free periods of the year, the hydrologic model contains essentially six adjustable parameters: three dimensional parameters describing the threshold and size of the reservoirs, two rate parameters relating hydrologic flux to the head in the linear reservoirs, and a routing parameter to determine the proportion of the flow from the upper reservoir that goes directly to the stream (Figure 10.6). In the initial application of the model to the Birkenes catchment (located in southern Norway), where only reactive solutes were included, parameter sets were identified that made physical sense and adequately reproduced the catchment hydrograph and chemographs. A strong correlation existed between discharge and solute concentration, with high flow being more acidic and aluminum rich. The model reproduced this pattern by routing acidic rainfall through the more acidic upper soil horizon. However, conservative tracers exhibited a much more dampened response, reflecting the predominance of pre-event water in runoff at Birkenes, as has widely been observed. Christophersen et al. (1985) found it difficult to reproduce both the dampened response of the conservative tracers and the rapid variations in the concentration of reactive solutes using manual model calibration.

To explore the model behavior more systematically, de Grosbois et al. (1988) developed a multi-signal automatic calibration methodology that used a weighted least squares objective function to determine the optimal parameter values for reproducing both the observed streamflow and oxygen-18 signal. For error-free artificial data, de Grosbois et al. (1988) found that the parameters could be determined uniformly better when both oxygen-18 and streamflow were used for calibration than when streamflow alone was used. At the best weighting for the tracer and streamflow signals, all six parameters could be determined to within 10% of their true value in 80% of the trials where the starting parameter values ranged from one-tenth to ten times the true parameter value.

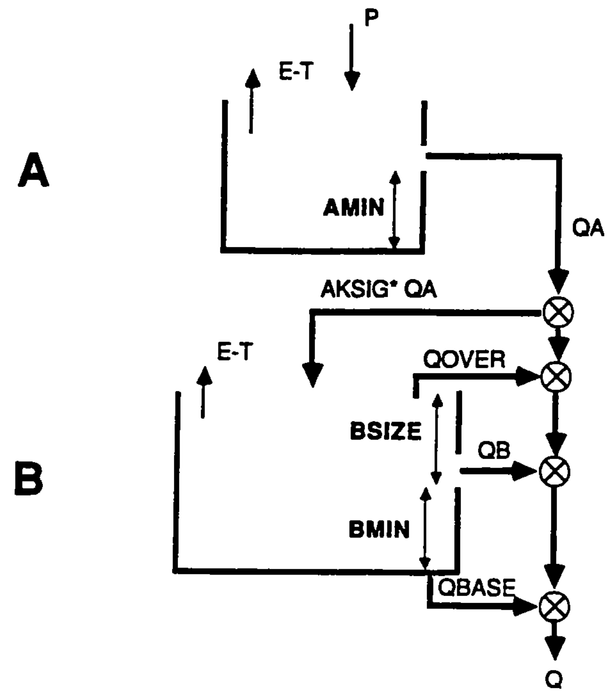

Figure 10.6. Schematic diagram of the hydrologic module of the Birkenes model (from Hooper et al., 1988). Outflow is generated from each of the two linear reservoirs (A and B) when a storage threshold (AMIN or BMIN, respectively) is exceeded. In addition, the B reservoir may generate overland flow (QOVER) if net inflow occurs when the maximum storage (BMIN + BSIZE) has been reached; it may also generate outseepage to baseflow (QBASE). The proportion of flow from the A reservoir (QA) that is routed to the B reservoir (instead of directly into the stream) is equal to AKSIG times QA, where AKSIG varies linearly from 1 (when the water level in B is less than BMIN) to a minimum of AKSMX (when the water level in B is at its maximum).

Hooper et al. (1988) applied this multi-signal calibration technique to real data from the Birkenes catchment. Inclusion of the conservative tracer improved the observability of the threshold parameters, a logical result because the tracer dynamics indicate the effective mixing volume in the catchment. Only the sum of the parameters, not two separate values as the model was originally posed, could be uniquely identified. Additional tracers would be required to identify more than one passive store. However, the tracer did not help to identify the routing parameter, which remained poorly constrained. Hooper et al. (1988) concluded that hydrologic and isotopic data could identify only a four-parameter model, which included only a single passive store and eliminated the routing parameter.

Kleissen et al. (1990) provided a more systematic examination of parameter identifiability in hydrologic models similar to the Birkenes model using both deterministic (Pohjanpalo's method) and stochastic (extended Kalman filter) approaches. This study attempted to understand what aspects of the data signal determined the parameter values, and therefore the most important field observations. This is termed an "a priori" model structural analysis that is not dependent upon the specific choice of parameter values as is an "a posteriori" analysis such as that performed by Hooper et al. (1988). Kleissen et al. (1990) demonstrate that if thresholds are included in the model, a tracer must be used to identify the model parameters. In general, they conclude that threshold and routing parameters are the most difficult to determine from the data, consistent with the results of Hooper et al. (1988). The deterministic method becomes algebraically intractable as the model becomes more non-linear. The extended Kalman filter can be applied to more complex models, but parameter values must be specified. Using this approach, Kleissen et al. (1990) found that inclusion of a tracer uniformly decreased the standard deviation of the parameter estimates.

Another hydrochemical model, the PULSE-model (Bergstrom et al., 1985) was modified to better simulate oxygen-18 concentration by Lindstrom and Rodhe (1986). The additional damping required to explain the oxygen-18 concentration was obtained by adding mixing in the unsaturated zone and storage volumes that do not affect runoff calculations. The storm response was modeled using a bypass mechanism that represents saturation overland flow.

10.4 Conclusions

Stable isotopes of oxygen and hydrogen have proven to be useful tools in determining the contribution of rainfall to stormflow, the residence time of water on catchments, and other aspects of watershed hydrology. The separation of contributions from event and pre-event (or "new" and "old") waters to stormflow adds a constraint on streamflow generation that physical (hydrometric) measurements never could. The large contribution of pre-event water to storm streamflow (usually 70-80% of hydrograph volume and peak flow rate) is entirely consistent with the importance of subsurface stormflow as documented by hydrometric studies on forested catchments before isotopes became widely used. In addition, isotopic studies clearly show that, through some combination of mixing and displacement, pre-event water usually makes up the bulk of stormflow, even discharging to streams through macropores and soil pipes. While stream pH and alkalinity are generally depressed during stormflows, the stable isotope data point out that this depression could be much more severe if subsurface mixing and flowpaths were different, and high-pH, high-alkalinity pre-event water made up less of storm streamflow.

Recent studies suggest that application of oxygen and hydrogen isotopes to hydrograph separation may be limited in many places and times by the significant temporal (intra-storm) variability in the isotopic composition of rainfall, and the spatial variability in the isotopic composition of subsurface (pre-event) water. This variability may impose severe constraints on the accuracy of hydrograph separations. One of the original attractions of two-component hydrograph separations was that they were based on spatially-integrated signals measured in the stream, potentially avoiding the logistical pitfalls (familiar from hydrometric studies) of point measurements on hillslopes. However, it now seems that subsurface sampling is necessary to evaluate the isotopic homogeneity of pre-event water. Fractional sampling of precipitation to gauge intra-storm isotopic variability is also beneficial, and is much simpler than spatially distributed sampling of pre-event water.

In development of lumped-parameter hydrologic models, stable isotopes have provided information that influenced the conceptualization of streamflow generation mechanisms and improved model calibration. Parameter identifiability was improved with tracers, but the model structures that could be supported by hydrologic and isotopic data remain quite simple. Other tracers, such as reactive solutes, could provide additional information for model calibration; however, inclusion of these solutes requires the introduction of additional model parameters. The salient question is whether the information provided by the additional data series is greater than the information required by the additional parameters. This question is an area of active research that requires advances in both numerical and analytical approaches to the problem of parameter identifiability.

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