32 Isotope tracers in catchment hydrology in the humid tropics

J. M. Buttle
Trent University, Peterborough, Canada
J. J. McDonnell
Oregon State University, Corvallis, USA

INTRODUCTION

Isotope tracers are an important tool for quantifying the age, origin and pathway of water to streams in headwater catchments. While used regularly in temperate and high latitude areas, applications of isotope tracer techniques in the humid tropics have been minimal to date. In the developing world, finances and logistics often preclude the use of traditional hydrometric measures of streamflow, groundwater dynamics and soil water recharge. Thus, isotopic tracers and isotopic hydrograph separations (IHSs) can serve as a valuable tool for extending our understanding of streamflow generation in poorly gauged areas (Shuttleworth, 2002), particularly in humid low latitude regions. They can also provide complementary information on water sources and pathways that are often required in order to draw conclusions about streamflow generation (reviewed by Bonell, this volume), effects of disturbance on tropical forest ecosystems (Bruijnzeel, 1990), or the closure of nutrient cycles in tropical forest ecosystems (Elsenbeer *et al.*, 1995).

The aim of this chapter is to provide an overview of what has been accomplished in isotope tracing studies (mainly in mid-latitude environments to date) as an impetus for those working in the humid tropics to consider the merits of this approach. While we do not advocate use of this technique exclusively in research settings, we argue that it can be a valuable approach in the 'toolkit' of land managers and catchment scientists working on hydrological processes related to land use change in humid tropical areas. This chapter presents a number of specific uses of isotope tracers in disturbed tropical systems, including general land use change detections, quantification of logging road runoff contributions to streamflow, as a tool in the design of model structures and model calibration for these systems, and as a means of quantifying a system's memory of disturbance through use of water age dating techniques. Although this chapter will focus on isotopic tracers, we will highlight the use of geochemical tracers (both conservative and non-conservative) and geochemical hydrograph separations (GHSs) as a means of complementing the insights into hydrological processes that can be obtained from isotopic tracers.

ISOTOPE HYDROGRAPH SEPARATION BASICS

The use of isotope tracers in hydrological research problems has grown rapidly. Aggarwal (2002) reports that a Georef search for the period 1965–1970 shows 650 papers using isotope tracers, while a search for the period 1995–2000 shows over 6500 papers using isotope tracers in groundwater studies alone. The main use of environmental isotopes in catchment hydrology to date has been in hydrograph separation (Burns, 2002). The use of these isotopes in hydrograph separation has been reviewed by Genereux and Hooper (1998) and Rodhe (1998). The reader is referred to Kendall and Caldwell (1998) for an excellent discussion of the geochemistry of environmental isotopes. Hence only the main issues pertaining to use of this tool in catchment hydrology will be covered here.

Isotopic hydrograph separations have generally been conducted using tritium (^{3}H or T), oxygen-18 (^{18}O) and deuterium (^{2}H or D) (Buttle, 1994). Oxygen-18 and D have been used in the majority of IHSs (Sklash, 1990) and, unlike T, they are stable and do not undergo radioactive decay. The ratios of ^{18}O and D to their more common counterparts in the hydrosphere (^{16}O and H) are 1:500 and 1:6700 (Drever, 1988). Determination of the abundance of stable isotopes in a water sample is based on isotopic ratios (e.g. $^{18}O/^{16}O$ and D/H). Abundance is reported as δ values in parts per

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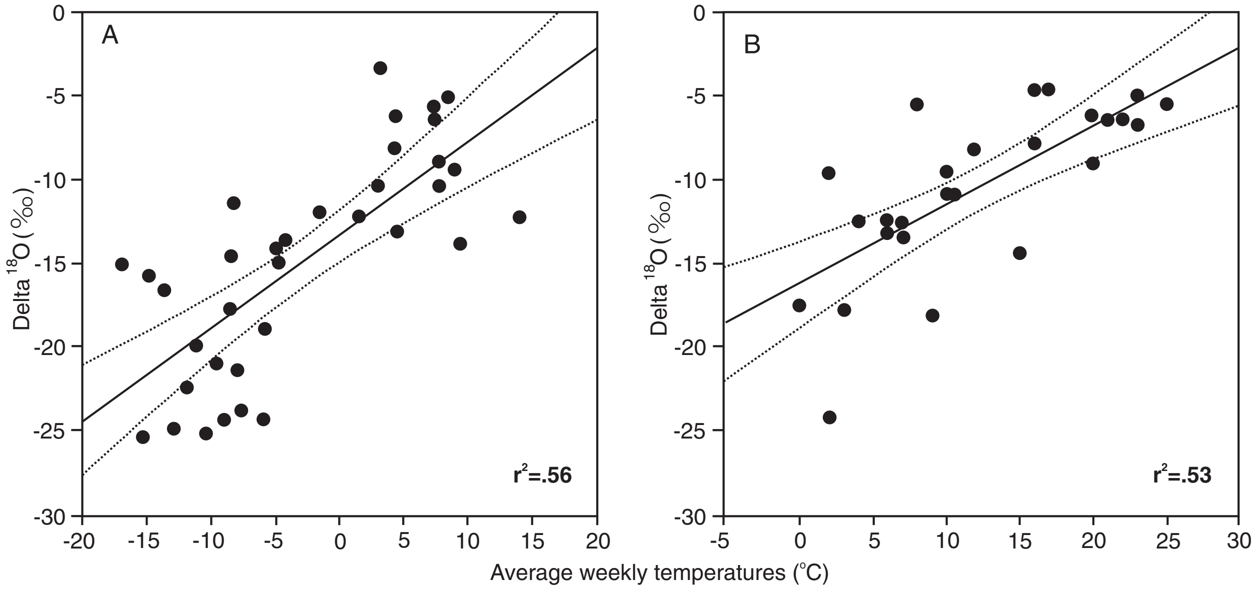

Figure 32.1 δ^{18}O vs. average weekly temperature (T_a) for precipitation collected at the Niwot Ridge, Colorado site (A) and at the North Platte, Nebraska site (B). The regression equation for the Niwot Ridge site was $\delta^{18}O = 0.55\ T_a - 13.3$ and for the North Platte site was $\delta^{18}O = 0.46\ T_a - 16.1$. (From Welker, 2000.)

thousand (‰or per mil) and δ values are calculated by:

$$\delta^{18}O or \delta D = (R_{\text{sample}}/R_{\text{VSMOW}} - 1) \bullet 1000 \qquad (32.1)$$

where R_{sample} is the ratio of the heavy to light isotope in the sample and R_{VSMOW} is the reference standard, which is Vienna Standard Mean Ocean Water (VSMOW) for ^{18}O and D (Kendall and Caldwell, 1998).

Isotope tracers have a number of unique virtues as water tracers in catchment studies:

1. They are applied naturally over entire catchments, thus avoiding problems of realistic application rates and extent of application associated with artificial tracers (Sklash, 1990).
2. They do not undergo chemical reactions during contact with soil/regolith at temperatures encountered at or near the Earth's surface (Drever, 1988).
3. They undergo fractionation during evaporation and condensation. During evaporation, water vapour is relatively depleted in the heavy isotopes while the remaining liquid water becomes progressively enriched in D and ^{18}O. Conversely, there is preferential movement of molecules containing the heavy isotopes to the liquid phase during condensation, leaving the vapour relatively depleted. Thus, meteoric water has negative δ values which have been found to decrease with surface air temperature (Figure 32.1), increasing latitude (Figure 32.2), increasing altitude, increasing distance of vapour transport (Figure 32.3), and increasing amounts of precipitation (Dansgaard, 1964; Ingraham, 1998).
4. Variations in the isotopic signature of precipitation are often dampened as water transits the unsaturated zone to the water table (Ingraham and Taylor, 1991), such that groundwater δ values may approach uniformity in time and space, and are changed only by mixing with waters of different isotopic contents (Sklash, 1990). This means that there is frequently a difference between the δ 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 its event (new) and pre-event (old) components:

$$Q_t = Q_p + Q_e \qquad (32.2)$$

$$C_t Q_t = C_p Q_p + C_e Q_e \qquad (32.3)$$

$$X = (C_t - C_p)/(C_p - C_e) \qquad (32.4)$$

where Q_t is streamflow; Q_p and Q_e are contributions from pre-event and event water; C_t, C_p and C_e are δ values in streamflow, pre-event and event waters, respectively; and X is the pre-event fraction of streamflow (Figure 32.4). The IHS in Figure 32.4 illustrates the partitioning of event and pre-event water in streamflow; it also demonstrates the consequences of δ in streamflow falling outside of the bounds set by C_p and C_e – namely, physically-unrealistic estimates of X that exceed 1 or are less than 0. In addition to the constraint that C_t values must fall between C_p and

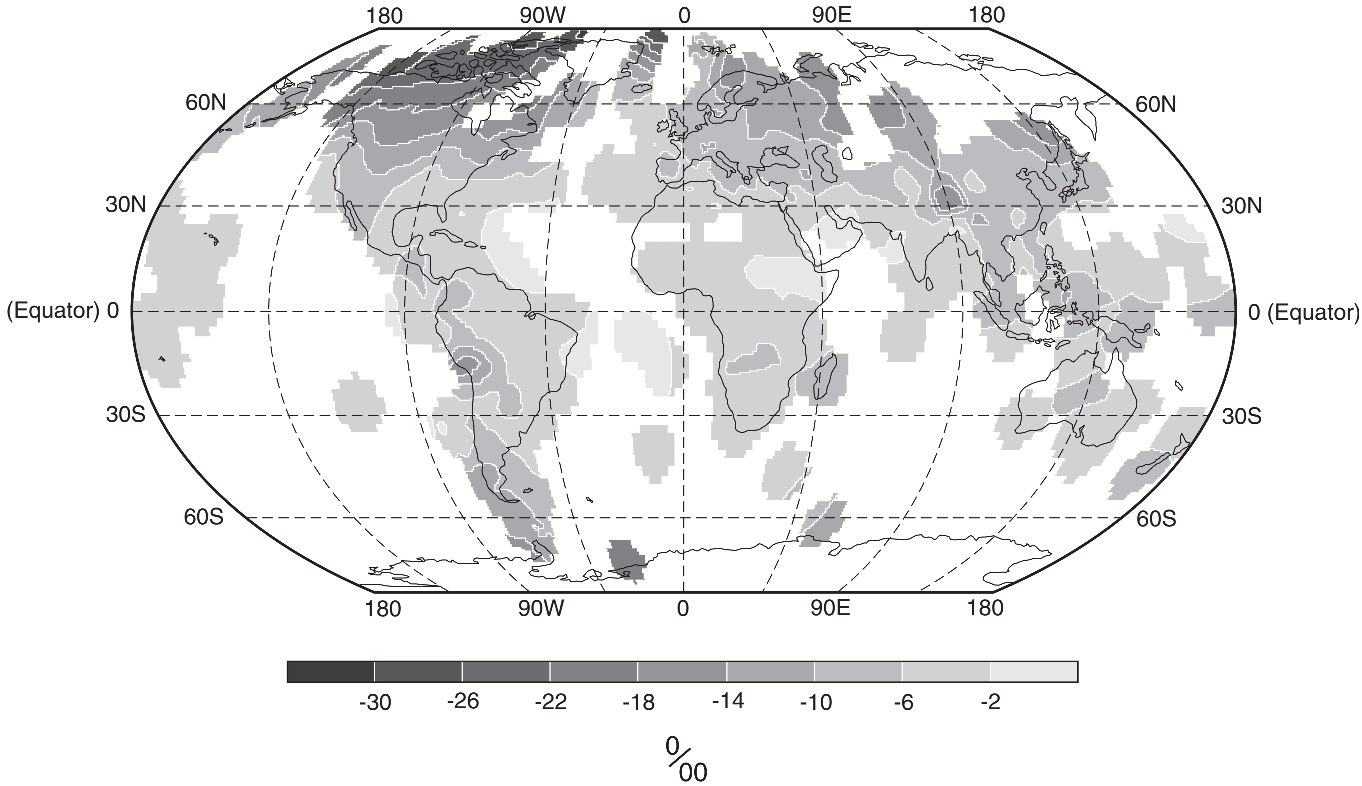

Figure 32.2 Weighted annual $\delta^{18}O$ in global precipitation. The latitudinal effect of decreasing $\delta^{18}O$ values with increasing latitude can be seen particularly clearly over North America. (From International Atomic Energy Agency, 2001.)

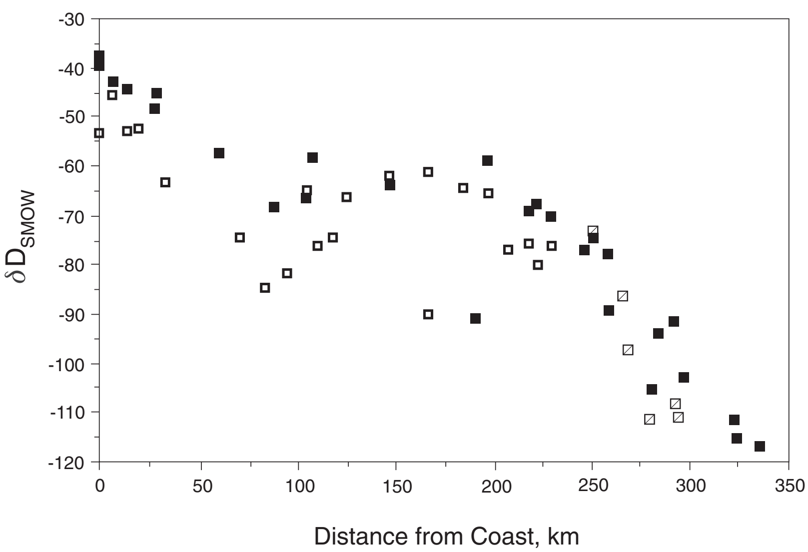

Figure 32.3 Weighted average δD of rain (open squares), snow (divided squares), and surface water and shallow groundwater (solid squares) vs. distance along a transect extending from the Pacific Ocean through central California and Nevada, USA. (From Ingraham and Taylor, 1991.)

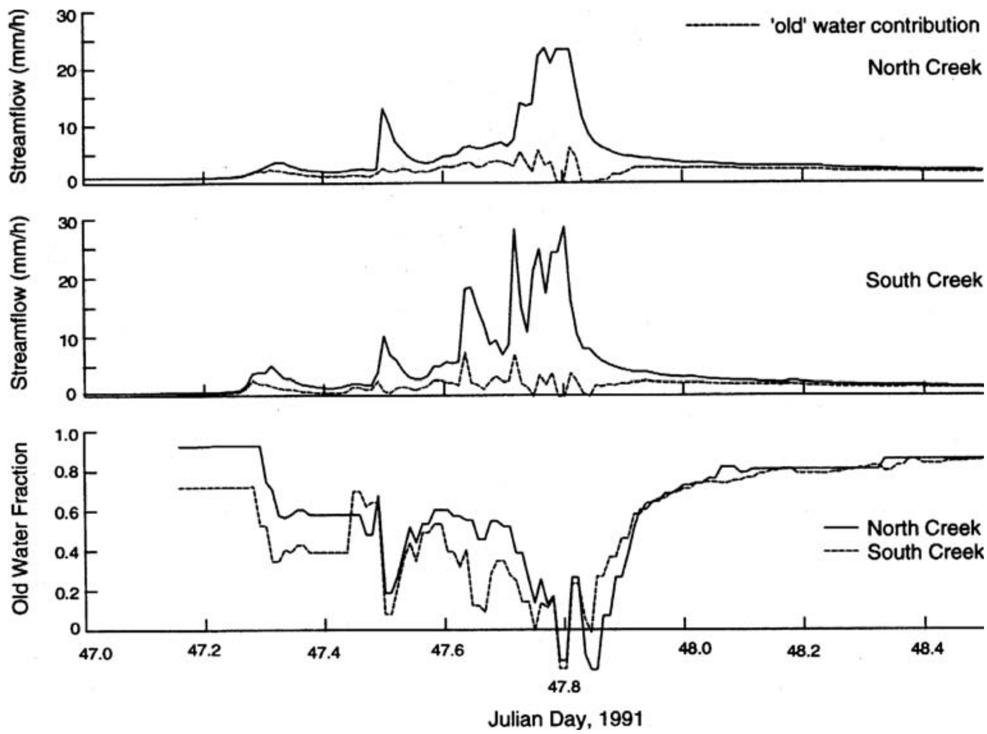

Figure 32.4 Isotopic hydrograph separation results from the Babinda catchments, Queensland, Australia. (From Bonell *et al.*, 1998.)

C_e to separate the streamflow hydrograph into event and pre-event components, the use of IHS is based on several key assumptions.

ASSUMPTIONS IMPLICIT IN THE TECHNIQUE

The assumptions that underlie the use of Eqns 32.2–32.4 to solve for the event and pre-event fractions of streamflow include:

1. There is a significant difference between the isotopic content of the event and pre-event components.
2. The isotopic signature of event water is constant in space and time, or any variations can be accounted for.
3. The isotopic signature of pre-event water is constant in space and time, or any variations can be accounted for.
4. Contributions of water from the vadose zone must be negligible, or the isotopic content of soil water must be similar to that of groundwater.
5. Contributions to streamflow from surface storage are negligible.

Rodhe (1987), Sklash (1990) and Buttle (1994), among others, have reviewed these assumptions and their implications for the reliability of IHS. The one assumption that appears to have been met in most if not all IHS studies is assumption (1). Nevertheless, there are aspects of the annual cycle of δ in precipitation in lower latitudes (examined below) that mean that this assumption may become particularly important in IHS studies in the humid tropics. Buttle (1994) has shown that most studies have been conducted in mid-to-high latitude environments. These often experience pronounced annual oscillations in the isotopic signature of precipitation, which increases the possibility that for any given event there will be a significant difference between δ for the precipitation event and that in pre-event water, the mean δ of which approximates the mean δ of annual precipitation (Clark and Fritz, 1997; Gremillion and Wanielista, 2000).

Several early studies that employed IHS did not pay excessive attention to whether the remaining assumptions had been violated. The isotopic signature of event water was often represented by samples from a single rain gauge, snowcore or snowmelt sample that may not have been obtained from within the catchment (Unnikrishna *et al.*, 2002). Bulk samples were employed in many cases, necessitating the frequently-untested assumption that temporal variations in event water δ were insignificant. Precipitation in many IHS studies is measured and sampled at open sites. This presents a problem when using IHS in forested catchments, where interception has been shown to result in isotopic enrichment of precipitation (Saxena, 1986; DeWalle and Swistock, 1994; Brodersen *et al.*, 2000) which may reduce the difference between the isotopic content of the event and pre-event components to such a degree as

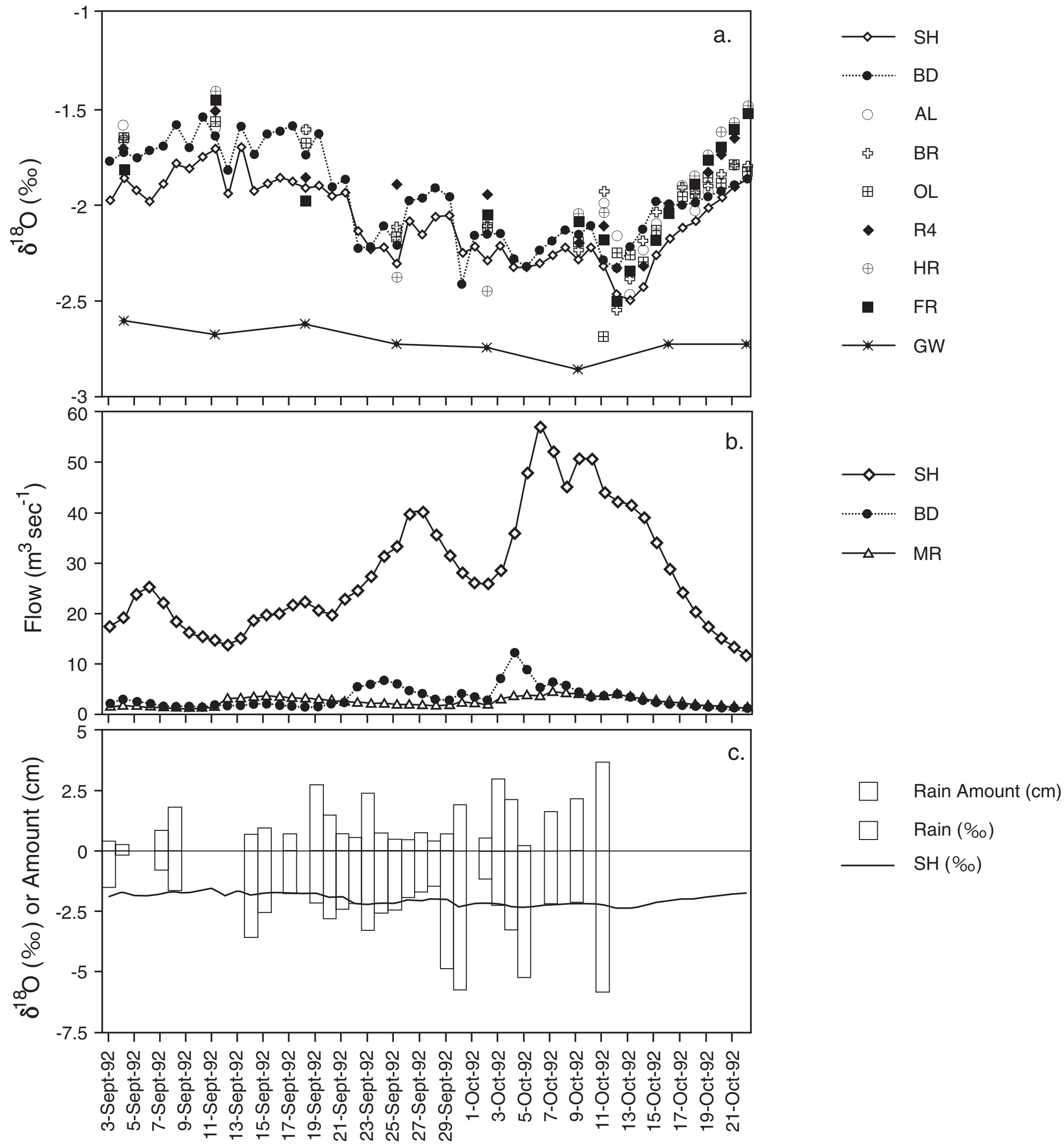

Figure 32.5 Weekly mean groundwater (GW) $\delta^{18}O$ and the $\delta^{18}O$ in river water sampled at various stations in the Econolockhatchee River catchment, central Florida, USA. (From Gremillion and Wanielista, 2000.)

to preclude hydrograph separation. There has been considerable work documenting spatial and temporal variations in event water δ at the scale of small catchments (e.g. McDonnell *et al*., 1990; DeWalle and Swistock, 1994; Bariac *et al*., 1995). Many initial IHS studies tested the hypothesis that pre-event water δ was constant in time and space. Sklash (1990) argued that baseflow δ is the best index of C_p on the grounds that baseflow integrates the δ of near-stream groundwater that is likely to reach the stream during an event. This assumption has been supported by the close correspondence between groundwater and baseflow δ observed in some studies (e.g. Hooper and Shoemaker, 1986; Hill and Waddington, 1993). Conversely, this argument has been called into question by documentation of substantial variability in baseflow δ along the stream channel (Bishop, 1991; Unnikrishna *et al*., in press) and by significant differences between δ in near-stream groundwater and in the baseflow that presumably integrates these groundwater δ values (Buttle *et al*., 1995; Bonell *et al*., 1998; Burns and McDonnell, 1998; Gremillion and Wanielista, 2000); Figure 32.5). Bonell *et al*. (1998) attributed these differences to variations in groundwater residence times in different parts of the catchment arising from geological complexity. Gremillion and Wanielista (2000) noted the importance of evaporative enrichment of river water in central Florida in producing differences between the isotopic signature of baseflow and groundwater. Such a process might be expected to be of greater significance to IHS studies in the tropics relative to humid mid-latitude environments.

Invocation of assumption (4) allowed some early workers (e.g. Sklash and Farvolden, 1979) to assume that X represented both the pre-event and groundwater fraction of total stormflow. However, this also necessitated the assumption that C_p has a constant value, such that streamflow δ returns to its pre-storm value once discharge declines to baseflow values (e.g. Bonell *et al*., 1990). Several studies have noted a shift in the δ of baseflow or groundwater in response to inputs during snowmelt or rainfall (e.g. Hooper and Shoemaker, 1986; Buttle *et al*., 1995; McDonnell *et al*., 1991a). Under these circumstances, C_p must reflect these temporal variations in baseflow or groundwater δ if X is to be interpreted as the groundwater fraction of discharge at the time of streamflow sampling.

A number of studies have documented substantial differences between δ in soil water and in groundwater or baseflow (e.g. Kennedy *et al*., 1986; DeWalle *et al*., 1988; Peters *et al*., 1995). The critical question is whether such water contributes to stormflow in significant quantities. There have been two basic approaches to addressing this question. In the first case, a soil water component of stormflow is inferred based on inadequate explanation of runoff sources using the standard two-component model (e.g. DeWalle *et al*., 1988; Ogunkoya and Jenkins, 1993; Hinton *et al*., 1994). A second approach uses hydrometric measurements to quantify soil water contributions to catchment streamflow (e.g. Buttle and Peters, 1997). In situations where significant contributions to stormflow from one or more additional flow components (e.g. soil water) have been identified, the standard mixing equations have been modified:

$$Q_t = Q_1 + Q_2 + Q_3 + \ldots + Q_n \tag{32.5}$$

$$C_t Q_t = C_1 Q_1 + C_2 Q_2 + C_3 Q_3 + \ldots + C_n Q_n \tag{32.6}$$

where Q_t = streamflow

Q_n = discharge of a particular runoff component
C_t = tracer concentrations in streamflow
C_n = tracer concentration of a particular runoff component

These equations can be solved using matrix algebra. The important point to note is that solution of the expanded mixing equations requires additional constraints and increases output uncertainty. In the case of solution for three flow components (e.g. event water, soil water and groundwater), either a second tracer or a physical measurement of flow from one component is required (Genereux and Hooper, 1998). A number of studies used a stable isotope tracer in conjunction with a geochemical hydrograph separation (GHS) to identify contributions from three flow components (e.g. Wels *et al*., 1991; McDonnell *et al*., 1991b; DeWalle and Pionke, 1994; Hinton *et al*., 1994). Unlike isotopic tracers, geochemical tracers provide information about hydrological flowpaths, provided the kinetics of tracer reactivity in the subsurface are known (Burns and McDonnell, 1998; Burns *et al*., 2001). A few studies have tried to quantify flow for a particular component – the best example being that of DeWalle *et al*. (1988), who estimated the rate of channel precipitation (direct supply of event water to streamflow) as the product of throughfall and stream surface area. The latter was estimated using a regression relationship derived from measured stream surface areas and corresponding streamflow rate. In the event that such hydrometric measurements are not available, n tracers are required to separate stormflow into $n + 1$ components.

Many initial IHS studies explicitly avoided catchments that possessed appreciable amounts of surface storage (e.g. lakes, ponds, wetlands). This appears to have been well advised, since several studies (e.g. Buttle and Sami, 1992; Hill and Waddington, 1993; Metcalfe and Buttle, 2001) have shown that mixing within wetlands can complicate interpretation of results from traditional two-component IHS. Although wetlands sometimes serve as a complicating factor in IHS, the enrichment of wetland water resulting from surface water evaporation may serve as an additional tracer through a hydrological system. Burns and McDonnell (1998) used departure from a local meteoric water line (i.e. the linear relation between ^{18}O and D) as a way to quantify wetland influences on water at the catchment outlet (Figure 32.6). They found that evaporation from a beaver pond caused a seasonal decrease in the slope of the meteoric water line for streamflow that was absent in a nearby catchment that did not contain any wetlands. This evaporative enrichment would be accompanied by an increase in solute concentrations in water held in the beaver pond, and such an evolution in isotopic and geochemical signals has implications for both IHS and GHS, especially in terms of assumptions (2) and (3) noted earlier.

The increased awareness among practitioners of IHS of the need for clear evaluation of the degree to which the underlying assumptions have been satisfied has been accompanied by explicit error analysis of IHS results (beginning with Rodhe (1987)). Genereux (1998) provided a first order uncertainty propagation approach to such an analysis, and showed that decreasing difference between C_e and C_p results in a marked increase in the uncertainty associated with resolving the contributions of these components to C_t. Both this approach and the Monte Carlo method of Bazemore *et al*. (1994) assume that the variability in the flow components signatures can be represented as normal distributions. Joerin *et al*. (2002) avoided this restriction in their analysis of statistical uncertainty in hydrograph separations (due to isotopic

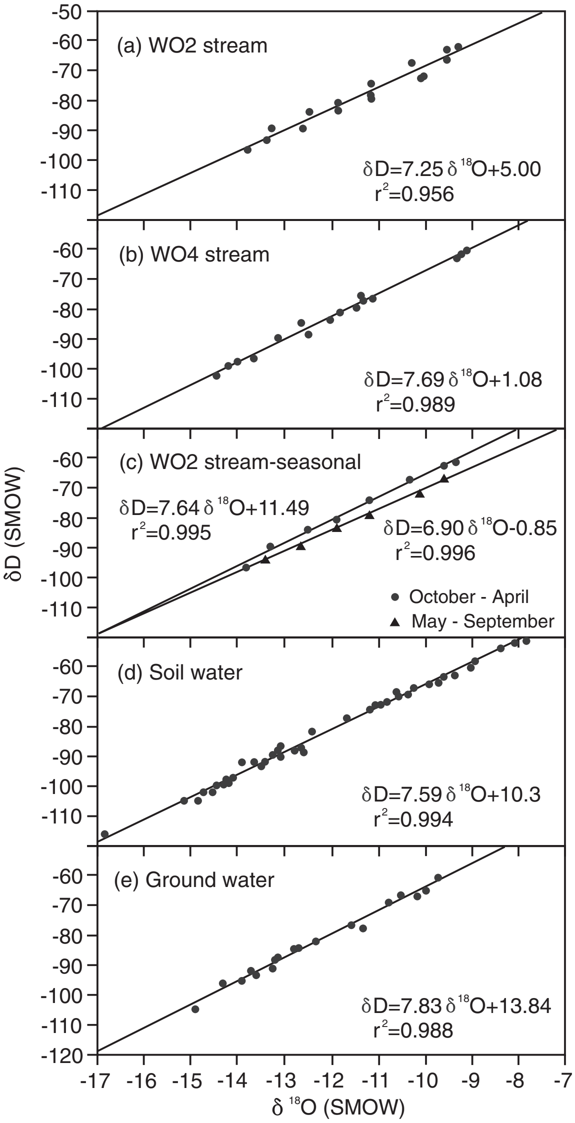

Figure 32.6 Meteoric water lines of δD vs. δ^{18}O in study catchments in northern New York, USA: (a) aggregate data for the catchment containing a beaver pond (WO2); (b) aggregate data for the catchment without a beaver pond (WO4); (c) seasonal data for the catchment containing a beaver pond (WO2); (d) soil water; (e) groundwater. (From Burns and McDonnell, 1998.)

and chemical variability of flow components) by combining a Monte Carlo approach with component frequency distributions determined directly from field samples. They also distinguished between statistical uncertainty and 'model uncertainty', which is affected by model assumptions such as temporal uniformity of flow component signatures.

All of these studies showed that spatial and temporal variability in isotopic end-member signatures can introduce substantial uncertainty in the estimated flow components. It is critical to take such uncertainty into account when interpreting hydrograph separation results in terms of physical processes operating in the catchment. An example would be the attempts to estimate event water fluxes via subsurface flowpaths through the simultaneous use of isotopic and geochemical (e.g. silica) tracers (e.g. Wels *et al*., 1991). Here, D was used in an IHS to separate event and pre-event water in a mid-latitude forested catchment during snowmelt. A concurrent GHS using silica as a tracer was used to separate the hydrograph into surface and subsurface flow components. The subsurface flow fraction was found to exceed the pre-event water component, and was interpreted as evidence for the movement of event water via subsurface pathways. However, a complete error analysis of IHS and GHS results in the same catchment during a spring rainstorm indicated substantial overlap between the estimated pre-event and subsurface flow components, suggesting that there were no grounds for inferring such event water fluxes *solely on the basis of the tracer results* (Buttle and Peters, 1997). This illustrates the need to constrain our inferences of processes using hydrometric or other data.

Although we take a critical view of the hydrograph separation assumptions and review some situations in which they have been shown to be unsupported, we do not seek to dissuade scientists from the use of IHS. Quite the opposite – IHS provides valuable insights into hydrological processes in catchments even in situations where one or more of the key assumptions has been shown to be violated. The true usefulness of IHS is in using hydrograph separations to the level of accuracy warranted by the approach, and not to read more precision into the results of IHS than is realistic. Current as well as potential users of the IHS approach would be well-advised to bear Fretwell's Law in mind:

> 'Warning! Stable isotope data may cause severe and contagious stomach upset if taken alone. To prevent upsetting reviewers' stomachs and your own, take stable isotope data with a healthy dose of other hydrologic, geologic, and geochemical information. Then, you will find stable isotope data very beneficial' (Kendall and Caldwell, 1998, p 52).

FINDINGS IN SMALL CATCHMENTS TO DATE

What we know

Perhaps the most important overall outcome from work in small catchments to date is the general finding that stormflow in many environments is dominated by pre-event water. Buttle (1994) provided an initial review of literature results from IHS studies, and this was updated by Richey *et al*. (1998). There is a great range in pre-event water fractions (X) of stormflow for various catchment sizes, land uses and event types (Shanley *et al*., 2002). Despite this variability in X, two salient points have emerged. The first is that X is generally smaller for catchments with land uses (e.g. urban – Halldin *et al*., 1990; Buttle *et al*., 1995; Gremillion *et al*., 2000) or surface types (e.g. permafrost – Cooper *et al*., 1991; Metcalfe and Buttle, 2001) that promote the contribution of surface runoff to stormflow production through such mechanisms as Horton overland flow. These areas would be likely to generate a greater event water fraction of stormflow as a result of these mechanisms. Secondly, X is generally smaller in forest catchments in humid temperate climates during spring snowmelt as a result of a greater tendency for surface runoff from frozen soils and maximum extents of saturated near-stream areas. This finding would initially seem to be of little or no relevance to conditions in the humid tropics. Nevertheless, the observation that X tends to decrease with catchment wetness is important, such that humid tropic catchments that experience an annual cycle in precipitation amount might also produce intra-annual variations in X.

What we think we know

In terms of scale effects on new/old water partitioning, the results are equivocal. While some have found increases in new water percentages with increasing catchment size (Shanley *et al*., 2002; McDonnell *et al*., 1999) others have found the opposite (Brown *et al*., 1999). McGlynn *et al*. (2002) used tritium (T) to define the mean residence time (MRT) of water in the catchment, and tested the hypothesis that baseflow MRT increases with increasing absolute catchment size. The Maimai catchments where they worked are, relative to many catchments around the world, simple hydrological systems with uniformly wet climatic conditions, little seasonality in temperature and precipitation, uniform and nearly impermeable bedrock, steep short hillslopes, shallow soils, and well-characterised hillslope and catchment hydrology. As a result, this was a relatively simple system and an ideal location for new MRT-related hypothesis testing. While hydrologists have used T to estimate water age since the 1960s nuclear testing spike, atmospheric T levels have now approached near-background levels and are often complicated by contamination from the nuclear industry. McGlynn *et al*. (2002) were able to use results for T sampled from the Maimai catchments in nuclear industry-free New Zealand. Because of high precision analysis, near natural atmospheric T levels and well-characterised rainfall T inputs, they were able to estimate the age of young (i.e. less than three years old) waters. Their results showed no correlation between MRT and catchment size. However, MRT was correlated to the median sub-catchment size of the sampled catchments, as shown by landscape analysis of catchment area accumulation patterns of McGlynn and Seibert (2003). Their preliminary findings suggest that landscape organisation, rather than total area, is a first-order control on MRT and points the way forward for more detailed analysis of how landscape organisation affects catchment runoff characteristics.

Some hydrologists have argued that the general observation that pre-event water often makes a significant contribution to stormflow has promoted a paradigm shift in hydrological thought. We question if this is in fact the case. There is abundant evidence from the hydrological modelling literature to suggest that IHS results have not been incorporated into many current catchment-scale hydrological models. The view that one's model captures the real-world processes correctly if one 'fits' the hydrograph correctly still persists. Some hydrologists have apparently forgotten, or never learned, the point that was well captured by Hooper (2001, p 2040): 'Agreement between observations and predictions is only a necessary, not a sufficient, condition for the hypothesis to be correct'. Seibert and 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 content on the catchment than we use for calibration of a model. While modellers often appreciate the need for 'hard data' for the model calibration process, there has been little thought given as to how modellers might access this 'soft' or process knowledge, especially that derived from isotope tracer studies. Seibert and McDonnell (2002) presented a new method whereby 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). They achieved very good fits for the three-box model when optimising the parameter values with only runoff ($R_{\mathrm{eff}} = 0.93$). However, parameter sets obtained in this way showed in general 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 R_{eff}-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 soft data (like, for instance, the new water ratio) 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 behaviour based on the information content of the isotope approach.

WHAT WE NEED TO KNOW: HUMID TROPICS

Perhaps the paradigm shift in conceptualising the rainfall-runoff process from one of event water dominance to pre-event water dominance is limited in geographical scope. The pre-event water paradigm seems to hold in environments where infiltration excess overland flow is relatively rare. However, the intense rainfalls that may occur in some parts of the humid tropics may mean that saturation (and even infiltration) excess overland flow may be more prevalent in forests than in the western European and North American studies that have used environmental isotopic tracers (Elsenbeer, 2001).

Work with tracers in the humid tropics to date has been limited and has focused on attempts to link flow components estimated using environmental isotopic tracers to causal hydrological processes. Bonell *et al*. (1998) used a relatively-extensive hydrometric record in the Babinda catchments in northeastern Australia to estimate seasonal changes in catchment storage. This assisted in the interpretation of catchment responses to tracers at various times of the year. Many IHS studies employ a moving average of the isotopic signature of rainfall composition to serve as the event water signature. ‘Such a moving average is equivalent to assuming a well mixed store for event rainfall, with a size that is large compared to runoff, and hence mean residence times that are large compared to the length of the event’ (Bonell *et al*., 1998, p 360). Based on hydrometric data demonstrating the exceptionally-rapid response times of the Babinda catchments, Bonell *et al*. argued against the use of such a moving average, proposing instead that event water δ should correspond to the composition of current rainfall, lagged by a constant amount. They documented the role of rainfall intensity in controlling a shift from a ‘first-in – first-out’ routing to a ‘last-in – first-out’ routing as slower intensity pathways are short-circuited (Figure 32.7).

Bariac *et al*. (1995) employed a combined isotopic, geochemical and hydrometric approach to streamflow generation in two small catchments in French Guiana. They observed highly-variable $\delta^{18}O$ in rainfall during short time intervals that exhibited a temporal variability that was similar in magnitude to spatial variability in soil water δ. These soil water δ profiles indicated rapid infiltration in the upper soil, followed by slower infiltration and homogenisation of input δ signatures deeper in the soil. The authors went on to identify streamflow contributions from these various soil layers.

A further example of relevant work in the humid tropics is that of Elsenbeer *et al*. (1995) and Elsenbeer and Lack (1996) in western Amazonia. This work did not employ environmental isotopes as tracers; nevertheless, its use of geochemical tracers and the conclusions that were drawn are of relevance to IHS studies in tropical catchments. The study showed the benefit of reconnaissance studies in guiding subsequent hydrometric and hydrochemical studies. At the same time, it identified the importance of overland flow as a distinct end-member in any hydrograph separations that would be conducted in this landscape (see Bonell, this volume).

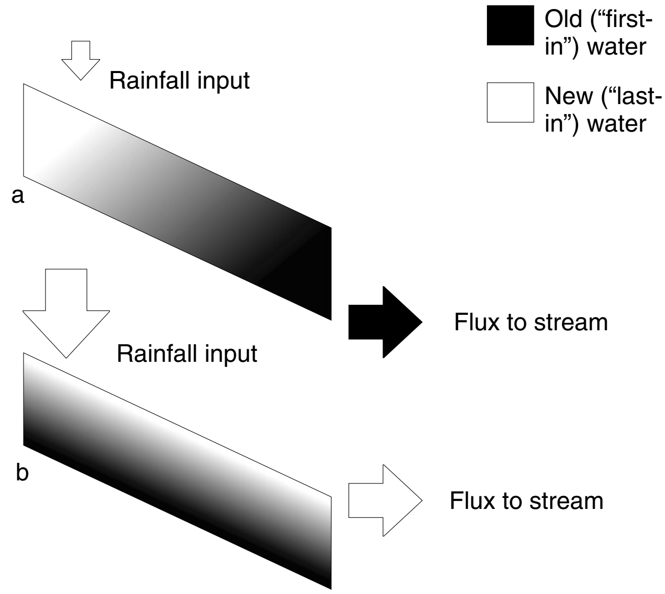

Figure 32.7 Schematic representation of the short-circuiting mechanism proposed by Bonell *et al*. (1998) for the Babinda, Queensland catchments. Under low-intensity rainfall inputs, slope water fluxes to the stream channel are dominated by old (‘first-in’) water moving via relatively deep subsurface slope pathways (a). This process has been referred to as translatory flow by Hewlett and Hibbert (1967). Under high-intensity rainfall inputs, new (‘last-in’) water moves quickly to the stream channel via more-conductive near-surface pathways, and dominates slope water fluxes to the channel (b). This effectively ‘short-circuits’ the translatory flow process, allowing new water inputs to bypass earlier water inputs stored deeper in the soil profile on the slope.

A consensus?

Beyond the general importance of pre-event contributions to stormflow, what can we agree on with regard to the results of IHS studies? First, we must recognise that the issue of equifinality (the same outcome can be generated by a range of alternative processes) applies to the interpretation of IHS results. Buttle (1994) has reviewed the various mechanisms that may be responsible for the rapid delivery of significant quantities of pre-event water to the stream channel, and concluded that the isotopic response of a catchment may be the result of several hydrological processes.

These can vary in their degree of importance both spatially and temporally. The prospect of equifinality undermines (perhaps fatally?) attempts to infer intra-catchment processes based on the isotopic responses at the catchment outlet. It also provides a compelling case for integrating isotopic tracers with other tracers as well as hydrometric techniques to constrain a process interpretation more fully. Second, we are not really advancing hydrological science appreciably by using IHS *by itself* in humid temperate environments (Bonell *et al*., 1998; Rice and Hornberger, 1998; Burns, 2002). We suspect that the same comment would apply if we were to use IHS alone in the humid tropics. Third, we cannot infer the correct hydrological pathways from the stormflow hydrochemical (or isotopic) signal *alone* (Elsenbeer *et al*., 1995); we must combine isotopic and geochemical tracers with hydrometric measurements. Fourth, IHS and GHS studies are essentially black-box approaches that assume that flowpaths and other hydrological properties are distributed homogeneously and that input waters have uniform isotope and chemical compositions (Kendall *et al*., 2001). As Kendall *et al*. (2001) note, these assumptions 'are often adequate for general characterisation of catchment response to bulk storms, but separations made using them do not have sufficient resolution to help answer questions about intrastorm changes in flowpaths and water sources, and processes occurring along the various flowpaths' (p 1878).

RESEARCH AND TECHNICAL ISSUES THAT REMAIN TO BE ADDRESSED

There are a number of conceptual and methodological challenges facing the linkage of isotopic tracers, geochemical tracers and hydrometric evidence (Uhlenbrook *et al.*, 2003). These challenges apply to the use of the IHS approach in both temperate and tropical environments. They require us to obtain answers to the following questions:

How important are processes acting parallel or sub-parallel to the stream channel in controlling its isotopic response?

Many of our conceptual models of streamflow generation envisage that the delivery of water via various pathways from the hillslope to the stream channel occurs normal to the channel margin, and often fail to consider the role of processes operating in the channel itself. Nevertheless, it is increasingly recognised that complex exchanges of water between the stream and its bed and banks may occur as hyporheic exchange during flow along the channel (Bencala, 2000), and such exchanges might be expected to alter the isotopic signal of slope runoff from point of entry to the channel to the sampling point at the mouth of the catchment. This presents both a challenge and an opportunity. The challenge is determining to what extent mixing processes in the hyporheic zone encourage divergence between flood wave and water particle travel times. This relates to the issue of hydrological linkages between landscape elements that is addressed in a subsequent section of this chapter. The opportunity is the potential to use isotopic tracers to help us distinguish between the residence times of water on hillslopes and in the hyporheic zone. Knowledge of the latter would be particularly valuable in studies of stream ecology, given the dependence of such key ecological metrics as DOC and dissolved oxygen on water residence time.

Examples of studies that have addressed the implications of channel processes for IHS results include Bonell *et al*.'s (1998) observation of an initial rise in pre-event water at the start of each hydrograph pulse in the Babinda catchments in NE Australia. They discounted the role of groundwater ridging close to the main stream based on soil water content – matric potential data that did not support the presence of a tension-saturated capillary fringe. Instead, they opted for the mechanism suggested by Nolan and Hill (1990), whereby sudden upstream inputs of new water set up a flood wave composed of pre-event channel water which reaches downstream locations in advance of the translation of the subsequent event water. This process is distinct from the evaporative enrichment of streamflow during passage along the stream channel that has been observed by Sklash *et al*. (1976) and Gremillion and Wanielista (2000). Such enrichment would result in the overestimation of X in streamflow by shifting the δ in streamwater towards the groundwater isotopic signature, and should be considered when using IHS in situations where water residence times in the stream channel are appreciable (see below).

What is the most appropriate way to incorporate temporal variations in event water in IHS studies?

McDonnell *et al*. (1990) studied various approaches to treating temporal variations in the event water isotopic signature and their influence on IHS results, including the use of volume weighted means, incremental means and incremental input intensity. Nevertheless, each approach assumes that the δ of input water early in the event still exerts an influence on the stream water signature by the end of the event. This may be a realistic assumption when dealing with relatively short-lived storms of a few hours or days in duration. However, during long duration events (e.g. entire snowmelt periods), these initial water inputs could be exported from the catchment before the end of the event, and their δ should not have any influence on the stream water signature at that time. Joerin *et al*. (2002) used the unit hydrograph concept to approximate the progressive decrease in the influence of rainfall on the event water δ signal with time. Conversely, Laudon *et al*. (2002) proposed a 'runoff corrected event water' approach that bases the estimated input water δ at a given time on the amount of event water discharged from the catchment prior to that time. Nevertheless, both approaches are consistent with Bonell *et al*.'s (1998) call for the use of event water δ that corresponds to the lagged composition of current water inputs. We need to test these and other approaches over a greater range of basin and water input characteristics.

Does all the water that falls on saturated areas retain the signature of event water?

As Kendall *et al*. (2001) noted: 'In theory, rainfall that flows over the soil surface (as infiltration excess overland flow or saturation excess overland flow) or has been transported to the stream via preferential flow in the soil (as vertical bypass flow and/or lateral pipeflow) should be chemically 'new' (event) water' (p 1878). However, recent work questions the assumption that the near-stream saturated area is connected to the stream channel so that direct precipitation onto saturated areas (DPSA) can actually reach the channel unaltered. Crayosky *et al*. (1999) found that most overland flow moves only a few metres before infiltrating, such that the re-infiltration and re-exfiltration of event water inputs as DPSA may account for tracer data (both isotopic and geochemical) that shows a difference between the input signature and that of overland flow. Bonell *et al*. (1998) concluded that regions of lateral interflow and exfiltration in catchments will inevitably promote mixing of event and pre-event water within saturation overland flow, thus modifying the isotopic content of this flow. Observations in the Sleepers River catchment in Vermont, USA, suggest that the degree of mixing in the near-stream saturated zone varies down-valley, depending on the local rates of groundwater exfiltration into this zone (McGlynn *et al*., 1999). This mixing appears to change through the hydrological year.

What water is actually being sampled from standard soil water samplers?

DeWalle *et al*. (1988) found no statistically-significant difference in δ in samples collected from soil water samplers (assumed to favour matrix water) and from pan lysimeters (assumed to favour macropore water). Conversely, Leaney *et al*. (1993) argued that suction lysimetry preferentially removes soil water from the larger capillaries, and such samples should therefore be biased towards the δ of soil water moving through the profile via relatively rapid pathways. The question does not become any clearer when attempting to characterise the isotopic signature of hillslope runoff using soil water samplers. Thus, Buttle and McDonald (2002) showed that the chemistry of soil water sampled at the base of the soil profile using suction samplers on forested slopes with thin soil cover differs significantly from slope runoff moving in a thin layer above the soil-bedrock interface. Burns *et al*. (2001) suggested that this debate can be avoided completely by sampling soil water for IHS and GHS using throughflow trenches. This ensures the sampling of mobile hillslope water that actually has the potential to participate in stormflow generation. Whatever the approach, the effect of sampling on how end-members are defined and described is an important point to note in any study employing IHS methods. The humid tropics offer great potential for samples to be altered by evaporation before they can be extracted from a lysimeter or trench. Thus, extreme care must be taken to ensure that samples are isolated from evaporative enrichment in any sampling device.

Is the inclusion of additional runoff components warranted, or does it simply reflect a mathematical correction to apparently-erroneous IHS results?

Failure of the standard two-component IHS to describe flow components in a realistic manner may suggest that contributions from one or more additional flow components (e.g. soil water) be included. This call for the consideration of more than two flow components has been made in numerous IHS studies reported in the literature. However, these components need to be supported by independent observations of the hillslope processes; otherwise they simply reflect a mathematical correction to apparently-erroneous IHS results (Bonell *et al*., 1998). The key issue is our ability to define a priori what these additional components might be and to sample them adequately. Uhlenbrook and Leibundgut (2002) developed a conceptual catchment model by defining three components contributing to streamflow in the Brugga basin in Germany. They found that direct runoff (with a MRT of a few months), shallow groundwater (32 months MRT), and deep groundwater (MRT of 7.1 yr) could be blended to give the combined stream signal. Uhlenbrook and Leibundgut (2002) validated the model output with silica concentration data where each of the three components could be characterised by uniquely different silica end-member concentrations. It appears from their work that the combination of conceptual model development and runoff component characterisation may be a way forward for identifying what minimum set of components define any given hydrological system.

How do temporal and spatial variations in hydrological linkages between landscape units (slopes – riparian zone – stream) affect a catchment's isotopic and chemical response?

As Welsch *et al*. (2001) observed, we need to be able to quantify the processes that affect the spatial distribution of solute concentrations in source water throughout catchments if we are to predict the hydrochemical response to such perturbations as forest harvesting and climate change. Are we seeing biogeochemical resetting of solute signatures as hillslope runoff transits the riparian zone to

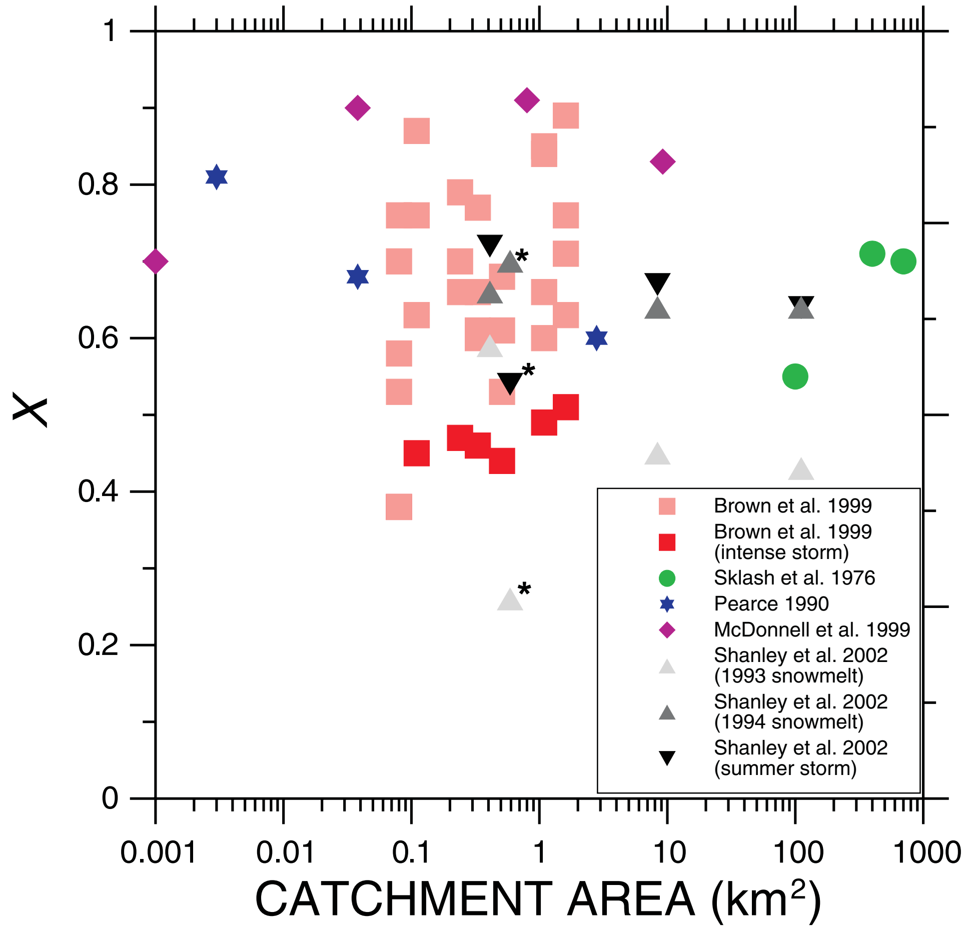

Figure 32.8 Reported pre-event water fractions in streamflow (X) vs. catchment area. The * associated with the Shanley *et al*. (2002) results indicates data from a small catchment largely in pasture. The other catchments from Shanley *et al*. (2002) were forested.

the stream (e.g. Robson *et al*., 1992; Hill, 1993) or simple mixing processes where a small volume of hillslope runoff is diluted by a larger volume of riparian storage during water transit (e.g. Burns *et al*., 2001)? We require further study of mixing and geochemical interactions in the riparian zone. Such interactions have important implications for our understanding of riparian dynamics, particularly in the context of the use of forested riparian buffer zones in attempts to mitigate the impacts of forest harvesting on aquatic ecosystems.

McGlynn and McDonnell (2003) examined the spatial sources and delivery mechanisms of DOC to streams. They examined the relationship between storm DOC dynamics, catchment landscape units and catchment scale to elucidate controls on DOC export dynamics. They focused on the controls on the characteristic hysteresis in DOC export dynamics (i.e. larger DOC concentrations on the rising relative to the falling limb of the discharge hydrograph), previously ascribed to a flushing mechanism. McGlynn and McDonnell (2003) found that the proportion of riparian runoff during the storm event was larger on the hydrograph's rising rather than falling limb, while the proportion of hillslope runoff was larger on the falling limb. The delayed response of hillslope runoff resulted in a disconnection between hillslope and riparian areas early in the event and thus greater DOC concentrations on the rising limb of the event water hydrograph. Later in the event, hillslope and riparian areas became connected once the hillslope soil moisture deficits were satisfied. They suggested that the relative timing of riparian and hillslope source contributions, and the connections and disconnections of dominant runoff contributing areas, are the first-order catchment controls on stream DOC concentrations and mass export.

How and why do IHS results vary with catchment scale?

As noted earlier, there is no agreement on how the partitioning between event and pre-event water in streamflow changes with catchment scale (Figure 32.8). Sklash *et al*. (1976) showed that X increased with catchment size for three catchments in southern Ontario. A similar result was found by Brown *et al*. (1999) for an intense rainstorm over six nested catchments in the Catskill Mountains of New York state. They attributed this to increased flux

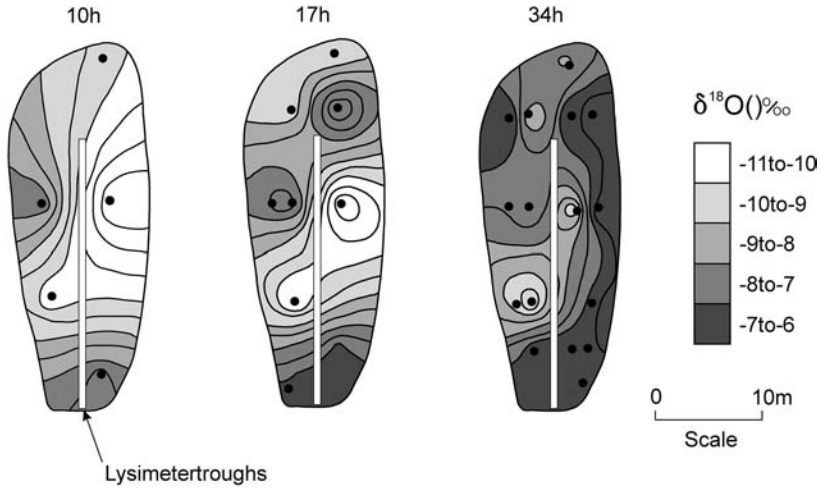

Figure 32.9 Inferred patterns of $\delta^{18}O$ in groundwater sampled from the Hydrohill experimental catchment, China, during a rainfall event that began on 5 July 1989. The dots indicate the locations of wells where $\delta^{18}O$ values were available at the indicated times since the start of 5 July. (From Kendall *et al*., 2001.)

of shallow perched pre-event groundwater in larger catchments. Conversely, Pearce (1990) suggested that larger catchment size at Maimai was associated with an increase in the relative size of saturated floodplains, which would enhance the event water contribution to stormflow. McDonnell *et al*.'s (1999) work at Maimai demonstrated greater pre-event water contributions as one moved from the plot to the small catchment scale, but a decrease in X as catchment scale increased from ~1 to ~10 km^2. Shanley *et al*. (2002) also found a decrease in X with increasing scale for forested catchments in Vermont USA for snowmelt and rainfall events, the exception to the general trend being a small catchment largely in pasture. Thus, further work is required to determine if there is a relationship between catchment morphology and the relative partitioning of event and pre-event water in stormflow, and the degree to which inter-catchment differences in land use, pedological and geological characteristics might influence any scale-dependence of IHS results.

FUTURE RESEARCH NEEDS

There are a number of avenues of study with considerable promise for the more effective use of environmental isotope tracers to help address the outstanding research issues raised above, including:

Controlled experiments that incorporate the use of environmental isotope tracers

These studies allow us to explore the role of specific processes and controlling factors by enabling manipulation of input rates and isotopic signatures. This lets us avoid the complication of marked temporal variations in the δ of precipitation inputs that often occur in natural events, and that may result in distinct event and pre-event water signatures that preclude IHS (Turton *et al*., 1995; Collins *et al*., 2000). Such studies vary widely in the degree of experimental control that has been employed. The Coos Bay experiment (Anderson *et al*., 1997; Montgomery *et al*., 1997; Torres *et al*., 1998; Anderson and Dietrich, 2001) involved artificial irrigation of a deforested hillslope on the west coast of the Oregon Coast Range in Oregon USA, and the examination of unsaturated and saturated zone processes and their implications for landscape evolution. Somewhat greater experimental control was exerted in the Gårdsjön covered catchment experiments in southwestern Sweden (Nyberg, 1995; Rodhe *et al*. 1996; Lange *et al*., 1996). Here a small catchment was roofed over to exclude natural precipitation inputs, and artificial precipitation of known intensity and composition was applied to the catchment surface. Finally, the Hydrohill experiment in China probably represents the extreme in controlled hydrological experiments (Kendall *et al*., 2001). A 490 m^2 artificial catchment was constructed, containing a detailed array of groundwater wells, runoff collectors and neutron probes. Kendall *et al*. (2001) were able to map changes in groundwater $\delta^{18}O$ during the course of the event (Figure 32.9). They obtained evidence that geochemical tracers (specifically, Cl^- and SO_4^{2-}) did not behave conservatively, that there were differences in the relative mobility of pre-event water within the catchment, and that agreement between GHS and hydrometric results was largely fortuitous. The results also suggested shifts from bypass flow to matrix flow during storms depending on rain intensity and amount of water stored in the soil zone. Kendall *et al*. (2001) argued that assessment of the impact of this process shift on IHS results requires more information on isotopic exchange rates in pore waters.

Estimation of water residence times at the point, slope and catchment scales using environmental isotopic tracers

There is abundant evidence from the literature demonstrating the important control that water residence time exerts on soil water, groundwater and streamflow chemistry. Isotopic tracers provide a valuable means of estimating MRTs at various scales in catchments. The benefits of such data are wide-ranging, and include DeWalle *et al*.'s (1997) suggestion that we can use these MRTs to estimate the length of time needed to observe catchment response to treatment or disturbance in the design of hydroecological monitoring programmes. Williard *et al*. (2001) state that we need to know the residence time of precipitation to assign a growing or dormant season $\delta^{18}O$ when estimating the proportion of atmospheric NO_3 deposition in streamflow samples. Bonell *et al*. (1998) go further, and contend that unambiguous IHS requires estimates of the travel time distribution for rainfall of a particular isotopic composition. McDonnell *et al*. (1999) attempted to implement such an approach whereby the age spectra of the new water were computed through the event. The approach of Rodhe *et al*. (1996) to estimating these distributions during controlled experiments at the Gårdsjön covered catchment is particularly promising, but may be difficult to apply in uncontrolled field conditions where marked short-term oscillations in input δ are the norm. These oscillations were partly responsible for the wide ranges in MRTs that provided significant fits to observed $\delta^{18}O$ time series in groundwater (Buttle *et al*., 2001) and soil water (Murray, 2003) during snowmelt in forested and clearcut landscapes in central Ontario, Canada.

The link between water residence times and IHS can be examined from another perspective. The standard IHS uses Eqns 32.2–32.4 as a steady state model that assumes negligible temporal changes in the volume and isotopic signature of channel storage. Gremillion *et al*. (2000) compared IHS results using steady state (SS) and non-steady state (NSS) solutions to Eqns 32.2–32.4 and found little difference in predicted pre-event water fractions from a catchment in central Florida. However, modelling studies showed increasing divergence between predicted pre-event water fractions with increasing water residence times in the stream channel. This issue needs to be considered when applying IHS to large catchments where flow time on hillslopes is small relative to the residence time of water routed along stream channels (Bras, 1990).

Integration of more advanced hydrometric techniques

Promising examples of this include work by Zollweg (1996) and Srinivasan *et al*. (2002), who have deployed arrays of surface saturation sensors in their studies of runoff generation on agricultural slopes in Pennsylvania, USA. By comparing estimated saturation overland flow to runoff recorded at flumes, Zollweg (1996) was able to estimate the amount of Horton overland flow and to gain insight into infiltration and exfiltration processes as overland flow moved downslope. Srinivasan *et al*. (2002) extended this work by documenting the temporal and spatial dynamics of surface saturation areas and surface runoff source areas (generating infiltration excess and saturation excess overland flow) in relation to water table dynamics and slope runoff. The complexity of stormflow generation revealed at the slope scale presents a disturbing challenge to the simplistic views of stormflow generation that are founded on isotopic, geochemical and hydrometric observations made at a few locations within a catchment and at the catchment outfall. There is a need to couple arrays of this type with tracer studies to address some of the challenges noted above.

Use of environmental isotopic tracers to identify process thresholds

Partitioning between event and pre-event water in slope runoff and catchment stormflow may have important implications for the transport of reactive substances such as dissolved organic matter (DOM) and atmospheric inputs of nitrogen from slopes to receiving water bodies. Repeated IHS studies in the same catchment under a variety of event and antecedent conditions have often noted changes in the partitioning of event and pre-event water, and several studies have attempted to account for such changes (e.g. Kendall *et al*., 2001; Buttle *et al*. 2001). In the case of the latter study, the proportion of pre-event water in runoff from a forested slope was observed to increase with antecedent soil water content, consistent with the hypothesised increase in translatory flow contributions to slope runoff during wet conditions (Hewlett and Hibbert, 1967). Conversely, transport of reactive ammonium (NH_4^+) applied to the slope during controlled irrigations was found to be greatest when event water supplied a significant fraction of slope runoff. This event water was inferred to travel via vertical and lateral preferential flowpaths, but was overwhelmed by pre-event water contributions to slope runoff when antecedent soil wetness was maximised. Greater documentation and understanding of the controls on shifts in the dominant processes operating at the slope and catchment scales is important to our ability to monitor and model catchment hydrochemistry.

Integration of isotopic and geochemical tracers and hydrometric techniques with greater consideration of topographic properties

We need to take advantage of the increased availability of digital topographic information to estimate where most of the hydrological/ hydrochemical action is going to take place in a catchment (e.g. Kendall *et al*., 1999). For example, topographic indices such as the $\ln(\alpha/\tan\beta)$ index of Beven and Kirkby (1979) has been used to estimate depth to groundwater (Moore and Thompson, 1996;

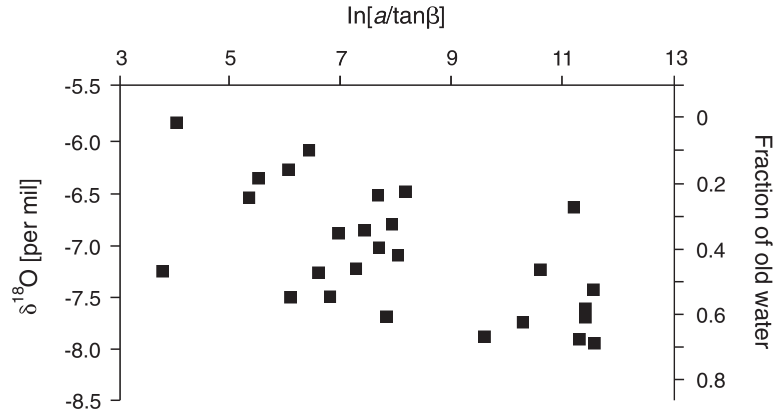

Figure 32.10 The $\delta^{18}O$ of all groundwater samples taken on 23 September 1991 from the Gårdsjön covered catchment experiments in Sweden vs. the Beven and Kirkby (1978) $\ln(\alpha/\tan\beta)$ topographic index, where α is upslope contributing area to a groundwater well location and $\tan\beta$ is the local gradient at that location. Corresponding fractions of groundwater consisting of old water are also indicated. (from Rodhe *et al*., 1996.)

Seibert *et al*., 1997) and to interpret spatial variations in the $\delta^{18}O$ of groundwater (Rodhe *et al*., 1996) (Figure 32.10). This information can be used to design field experiments to ensure that hydrologists get the greatest information return on their investment of time, effort and money. Concurrent with this work, we need to explore the use of different types of topographic data (e.g. surface topography vs. bedrock topography – e.g. Freer *et al*., 1997; 2002) and topographic indices (e.g. Burch *et al*., 1987; Barling *et al*., 1994; Chaplot *et al*., 2000).

Explicit integration of models into our study designs

The call for greater integration between field and modelling studies is an old one, but is still being made by hydrologists. A recent example of this is Hooper's (2001) point that we should adopt sampling strategies that might permit the generation of data that could then be used to test a range of models. Another view is to use tracer information and hydrograph separation results in the model calibration process. Seibert and McDonnell (2002) used the peak new water percentage as 'soft data' in a multicriteria model calibration exercise. This and other process knowledge helped to improve model simulations, where usually only hard data such as the continuous runoff signal are used to calibrate the model.

APPLICATION POTENTIAL OF IHS FOR LAND USE CHANGE STUDIES IN THE HUMID TROPICS

Potential problems facing application of IHS in the humid tropics

Figure 32.11 shows $\delta^{18}O$ in precipitation for Ottawa, Darwin, Manaus and Harare. Ottawa (mid-latitude) values vary during the course of the year by up to ~15‰. Conversely, low-elevation sites in tropical latitudes have an annual range in $\delta^{18}O$ in precipitation of ~10‰, which would reduce the potential of observing a significant difference between δ for the precipitation event and that in pre-event water. However, Gremillion and Wanielista (2000) found that a range in $\delta^{18}O$ for precipitation in central Florida of between −6.64 and −0.17‰provided sufficient variability between event and pre-event water signatures to permit IHS. In addition, the amplitude of the annual $\delta^{18}O$ cycle increases with altitude in the tropics, such that $\delta^{18}O$ in precipitation for Harare may be only slightly less than that in mid-latitude environments. This point is supported by work on the Table Mountain of South Africa funded through the International Atomic Energy Agency (IAEA) that indicates elevation increases from the coast to Table Mountain (3567 m) produce a clear 'signal' greater than might be expected based solely on latitudinal position. Seasonal changes in air mass type in the outer tropics may also result in promoting significant differences between event and pre-event δ signatures. For example, Barnes and Bonell (this volume) show a seasonal trend from generally lighter D values associated with the deeper (and colder) convection of monsoon disturbances towards heavier D signatures of 'warm rain' identified with clouds of the southeast trade winds that have higher temperatures at the condensation level. The low cloud temperatures associated with the high intensity, deep convection monsoonal disturbances resulted in an event water D signature that was much lighter than that of pre-event streamflow in Queensland, Australia (Bonell *et al*., 1998), thus permitting a successful IHS.

Changes in water flowpaths

Hydrograph separation and solution of Eqns 32.2–32.4 provides a basic description of water sources contributing to the stream.

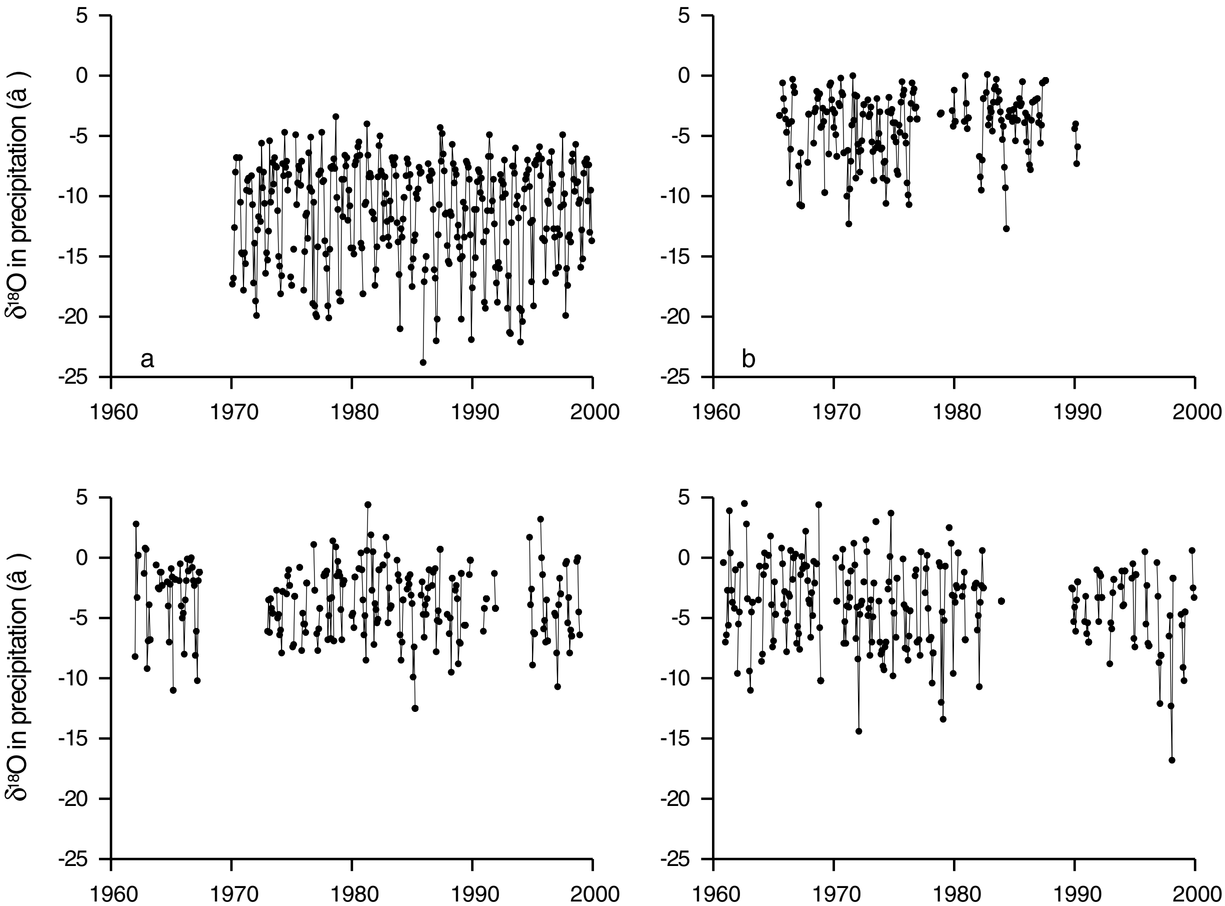

Figure 32.11 Time series of $\delta^{18}O$ in precipitation sampled at (a) Ottawa, Canada (114 m asl; 45.32°N latitude); (b) Manaus, Brazil (72 m asl; 3.12°S latitude); (c) Darwin, Australia (26 m asl; 12.43°S latitude); and (d) Harare, Zimbabwe (1471 m asl; 17.83°S latitude). Data from International Atomic Energy Agency/World Meteorological Organization (2001).

Furthermore, the relative proportion of old and new water before and after disturbance or land use change may be a useful change detection tool. While studies to date have been very few (but see Gremillion *et al*. 2000), the tool offers the potential to quantify changes in hydrograph *composition* after disturbance. In particular, the juxtaposition of labile nutrient tracers of flow path and stable isotope tracers of flow source can be a powerful tool for resolving water flow dynamics at the catchment scale. In some land-use change studies, alteration of surface conditions due to compaction, downed woody debris, etc., may force water to move laterally at shallower depths than it did prior to disturbance. Murray (2003) compared vertical profiles of mean residence times estimated from soil water $\delta^{18}O$ time series during snowmelt at forest and clearcut sites in central Ontario. This suggested a short-circuiting mechanism in clearcuts that restricted deep infiltration of inputs and diverted a portion of incoming event water laterally downslope, with important consequences for the quantity and quality of slope runoff reaching receiving waters (see also Bonell, this volume). The potential for forest harvesting to induce changes in water flowpaths was also suggested by Bariac *et al*. (1995), who used a combined IHS – GHS approach to examine differences in water flowpaths in forested and deforested (pasture) catchments in French Guiana. Peak flow from the forest catchment was largely via subsurface flow, whereas flow through the superficial soil layers dominated peak streamflow in the catchment with pasture land use. Brown *et al*. (1999) used analysis of DOC – $\delta^{18}O$ variations to quantify a shallow flow pathway through the organic layer on steep forested slopes in the Catskill Mountains of New York State. They showed that the combination of high DOC and rainwater-like $\delta^{18}O$ signatures could be used to determine that rain followed a shallow flowpath during intense summer thunderstorms. Similarly, Peters *et al*. (1995) used IHS to confirm that initial slope runoff over the forest organic mat during a spring rainstorm in central Ontario was predominantly event water. This flow was attributed by Buttle and Turcotte (1999) to the hydrophobicity of dry organic matter (Burch *et al*., 1989, Wilson *et al*., 1990) which promoted runoff over and through the organic 'thatch'. Buttle and Turcotte (1999) demonstrated that this overland flow decreased in quantity with antecedent soil wetness, hypothesising that a wetter litter layer would increasingly redirect event water inputs vertically into the underlying mineral soil.

Detection of forest road interception effects

Forest roads can affect the stormflow response of a catchment in a variety of ways (Ziegler and Giambelluca, 1997): (i) increased overland flow production and flow velocities on compacted road surfaces and disturbed roadside margins; (ii) interception of subsurface flow at cutbanks and re-routing via overland flow; (iii) capture and channelling of surface and subsurface flow by ditches and culverts; and (iv) capture and re-routing of surface water by erosion gullies initiated by the initial disturbance caused by the road. The standard two-component mass balance approach in Eqn 32.1 is well suited to applied problems such as the effects of forest road construction on water re-routing at the catchment scale. Resource managers often need to determine the possible increase in peak flow associated with forest harvesting and the presence of forest roads. Ditch flow can be separated using Eqn 32.1 into direct road runoff (event water) and intercepted subsurface flow from the cut back (pre-event water). This separation can be a valuable tool for quantifying these relative inputs at specific cross-drain and road culvert sections. Ziegler *et al*. (2001) were amongst the first to demonstrate the use of this approach in studies of forest road runoff in the humid tropics of Thailand, and Luce (2002) has called for increased use of hydrograph separation in land-use change studies involving roads.

Changing runoff composition as a result of suburban development

Wolman (1967) characterised the cycle of land use change in eastern North America following European settlement as a transition from forest to agriculture to woods and grazing to suburban and urban development that encompassed ∼150 years. However, the growth of urban and suburban areas in the humid tropics is faster than anywhere else on the planet, and forested areas adjacent to such cities as Kuala Lumpur, Bangkok and Manila are converted directly to residential and industrial uses without passing through phases of agriculture and reversion to forest cover prior to development. There are a variety of mitigation measures (e.g. infiltration swales, detention ponds) that can be used to ensure that suburban development does not result in significant changes to the pre-development hydrograph form. However, development may result in a shift in stormflow pathways from largely subsurface during the pre-development phase to overland and channelised flow after development (Buttle, 1990). This shift can have major implications for the coupling between the riparian zone and the stream channel, since subsurface flow often must transit the riparian zone before reaching the stream. This in turn has consequences for alterations in the retention, transformation and mobilisation of substances in the riparian zone following development, as well as the response of riparian hydroperiod and overall wetland health to changes in subsurface flow contributions (Gremillion *et al*., 2000). IHS provides a useful tool for identifying water sources in urban and suburban catchments, particularly if the link between event water generation and infiltration excess overland flow from modified surface cover can be made (cf. Halldin *et al*., 1990; Buttle *et al*., 1995). For example, Gremillion *et al*. (2000) performed IHS for rural and suburban sub-catchments of the Econlockhatchee River in central Florida. They noted greater event water contributions to stormflow from the suburban sub-catchment, which was attributed to an increased proportion of surface runoff in the storm hydrograph. This change in water flow paths to the river may alter groundwater flow through riparian zones, with implications for river water quality and riparian zone ecology (Gremillion *et al*., 2000). Information on event and pre-event water partitioning of stormflow can also assist in interpreting and modelling the export of surface-applied chemicals from catchments, such as radionuclides deposited in fallout from the Chernobyl accident (Halldin *et al*., 1990) and de-icing salts (Buttle *et al*., 1992). Therefore IHS is another tool that can be used by hydrologists to assess the overall hydro-ecological impacts of suburban development.

Quantifying where mixing occurs in the landscape

While much of the work reviewed in this chapter has focused on the stream signal as an integrated measure of catchment-wide mixing, more needs to be done to define where this mixing occurs, how riparian zones modulate runoff and solute load from hillslopes and how these discrete units mix from the headwaters to the catchment outlet. The potential of riparian zones to buffer hillslope runoff depends partly on the size of the riparian zone relative to the adjacent upland area. McGlynn and Seibert (2002) presented a simple approach for quantifying the local contributions of hillslope and riparian areas along a stream network based on digital elevation data, and computed such catchment characteristics as the distribution of riparian and hillslope inputs to the network, the variation of riparian area percentage along the network, and sub-catchment area distributions. They found that sub-catchments with areas <20 ha comprised 85% of the total catchment area contributing to streams near Maimai in New Zealand, while only 28% of the catchment's total riparian area was found along these small streams. In addition, the median riparian-to-hillslope-area ratio along these tributaries was only 0.06, indicating that the 'effective' riparian-to-hillslope-area ratio would be significantly overestimated by the average value of 0.14 for the entire 280 ha Maimai research area. This landscape analysis and discretisation approach may be highly effective in land use change issues in the humid tropics where terrain-based measures of sensitivity can be used to develop hypotheses to then be tested with isotope tracer approaches.

CONCLUSIONS

Isotope hydrograph separation studies have gone through two stages – unbridled use and enthusiasm for the technique, followed by careful reflection and consideration of the assumptions and limitations. Given that we are presumably passing through the second stage, we are now well poised for applying isotopic tracing techniques in new environments (like the humid tropics), especially for detecting quantitative shifts in hydrological processes in the context of land-use change. This chapter has outlined the basic principles surrounding the use and implementation of the IHS technique and the various assumptions and limitations associated with its use. The reader is advised to reflect on how these new approaches can be applied in the context of what is known about the runoff process in the humid tropics from their reading of the chapter by Bonell. We hope that new students and researchers will consider using isotope tracer tools as they seek to define a robust quantitative description of how their humid tropical catchments work.

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