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A look inside 'black box' hydrograph separation models: a study at the Hydrohill catchment

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Abstract:

Runoff sources and dominant flowpaths are still poorly understood in most catchments; consequently, most hydrograph separations are essentially 'black box' models where only external information is used. The well-instrumented 490 m^2 Hydrohill artificial grassland catchment located near Nanjing (China) was used to examine internal catchment processes. Since groundwater levels never reach the soil surface at this site, two physically distinct flowpaths can unambiguously be defined: surface and subsurface runoff. This study combines hydrometric, isotopic and geochemical approaches to investigating the relations between the chloride, silica, and oxygen isotopic compositions of subsurface waters and rainfall.

During a 120 mm storm over a 24 h period in 1989, 55% of event water input infiltrated and added to soil water storage; the remainder ran off as infiltration-excess overland flow. Only about 3–5% of the pre-event water was displaced out of the catchment by in-storm rainfall. About 80% of the total flow was quickflow, and 10% of the total flow was pre-event water, mostly derived from saturated flow from deeper soils. Rain water with high $\delta^{18}O$ values from the beginning of the storm appeared to be preferentially stored in shallow soils. Groundwater at the end of the storm shows a wide range of isotopic and chemical compositions, primarily reflecting the heterogeneous distribution of the new and mixed pore waters. High chloride and silica concentrations in quickflow runoff derived from event water indicate that these species are not suitable conservative tracers of either water sources or flowpaths in this catchment. Determining the proportion of event water alone does not constrain the possible hydrologic mechanisms sufficiently to distinguish subsurface and surface flowpaths uniquely, even in this highly controlled artificial catchment. We reconcile these findings with a perceptual model of stormflow sources and flowpaths that explicitly accounts for water, isotopic, and chemical mass balance. Copyright © 2001 John Wiley & Sons, Ltd.

KEY WORDS isotopes; hydrograph separation; isotope hydrograph separation; chemical hydrograph separation; runoff sources; Hydrohill; water flowpaths; mass balance; water budget

INTRODUCTION

Runoff sources and pathways are poorly understood in many experimental catchments (Bonell, 1998; Kendall and McDonnell, 1998). Most hydrograph separations are essentially 'black box' models where only external information is available—the amounts and/or compositions of the rain and baseflow inputs and the stream output. Such models allow quantification of catchment response to storm events but do not reveal how the catchment 'works'. The existence of spatial and temporal variability inside the catchment during storm events can pose substantial difficulties for the use of such models for tracing sources and flowpaths of water contributing to stormflow.

Hydrograph separation using naturally occurring stable isotopes (Sklash and Farvolden, 1979, 1982) and conservative tracers (Wels *et al.*, 1991) have advanced our understanding of the time and geographic sources of channel stormflow (Genereux and Hooper, 1998). Nevertheless, considerable debate still exists regarding

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the information provided by static end-member hydrograph separations (Harris *et al*., 1995) and the meaning of chemical *versus* isotopic tracer information (Rice and Hornberger, 1998; Richey *et al*., 1998). In general, we regard conservative isotope tracers ($\delta^{18}O$, $\delta^{2}H$, etc.) as indicators of water sources, and chemical tracers (Cl, SiO_2, etc.) and non-conservative isotope tracers ($\delta^{13}C$, $\delta^{87}Sr$, $\delta^{34}S$, etc.) as indicators of water flowpaths but only indirectly as indicators of water sources (Kennedy *et al*., 1986; Wels *et al*., 1991; Kendall *et al*., 1995; Kendall and Caldwell, 1998). Chemical hydrograph separation (CHS) also distinguishes between types of pre-event and event waters, but is more prone to interpretation problems because there is the possibility that the solute in question may be continuously reacting with matrix material along the flowpath instead of behaving conservatively (Bottomley *et al*., 1984; Wels *et al*., 1991; Burns *et al*., 1998).

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. Studies that compare CHS and isotope hydrograph separation (IHS) generally find no significant difference between calculated percentages of event and pre-event water, although there is some evidence that pre-event amounts calculated using chemical tracers may be slightly higher (Richey *et al*., 1998). Thus, it has been suggested that IHS may give only upper limits on the amounts of water from deeper subsurface flowpaths that may contribute to streamflow because event water travelling along deep preferential flowpaths, often at the soil–bedrock interface (McDonnell, 1990), may not pick up much of a dissolved load (Wels *et al*., 1991). Though several recent hydrometric investigations of hillslope runoff processes and flowpaths have addressed this problem (Peters *et al*., 1995; Anderson *et al*., 1997; Tani, 1997), few of them have been able to place the detailed mechanism in the context of water and isotope/chemical mass balance.

For both IHS and CHS, physical and chemical processes are estimated from knowledge of the amounts and compositions of the input appearing in the streamflow. This is essentially a black box approach—one that assumes flowpaths and other hydrologic properties are homogeneously distributed and that input waters have uniform isotope and chemical compositions. A two-component (i.e. two water sources) separation is made for a hydrograph:

$$f_{\mathrm{pe}} = \frac{C_{\mathrm{e}}C_{\mathrm{s}}}{C_{\mathrm{e}}C_{\mathrm{pe}}} = \frac{Q_{\mathrm{pe}}}{Q_{\mathrm{s}}} \tag{1}$$

$$f_{e} = \frac{C_{\mathrm{s}}C_{\mathrm{pe}}}{C_{\mathrm{e}}C_{\mathrm{pe}}} = \frac{Q_{\mathrm{e}}}{Q_{\mathrm{s}}} \tag{2}$$

where f is the fraction of total streamflow due to each component ($f_{\mathrm{pe}} + f_{\mathrm{e}} = 1$), Q is volumetric flow rate, and C_{pe}, C_{e}, and C_{s} are the concentrations of the isotopic tracer in pre-event, event, and sample water respectively. These equations are usually solved for the fraction of streamflow due to each component.

Several simple assumptions must be made to use these equations to solve for event f_{e} and pre-event f_{pe} water components. First and foremost, the event and pre-event waters must have distinctive compositions (C_{e}, C_{pe}). Genereux (1998) showed that ΔC, the difference $C_{\mathrm{e}} - C_{\mathrm{pe}}$, greatly affects the amount of uncertainty in tracer-based hydrograph separation. As ΔC increases, so does the quality of the separation. Other typical assumptions are that water stored in the unsaturated zone is either negligible in amount or similar in composition to groundwater or rain, and that rain and groundwater can be adequately characterized by constant compositions (Sklash and Farvolden, 1982). These simple assumptions are often adequate for general characterization 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. Concern about environmental problems, such as acid deposition, has focused attention on episodic behaviour in catchments, hence creating a demand for more accurate methods of hydrograph separation.

In the last decade, the validity of the simple assumptions has been evaluated by a number of investigators, including Sklash and Farvolden (1979), Kennedy *et al*. (1986), McDonnell *et al*. (1991), Genereux (1998), and Genereux and Hooper (1998). For example, within-storm changes in C_e can affect new water estimates in channel stormflow by up to 30% (McDonnell *et al*., 1990; DeWalle and Swistock, 1994). Though spatial variability in rainfall isotopic or chemical composition is usually negligible in small (<10 ha) research catchments, spatial variability of soil water and groundwater have been reported (Ogunkova and Jenkins, 1991; McDonnell *et al*., 1991; Kendall and McDonnell, 1993).

Measuring, quantifying and accounting for this variability has been one of the most intractable problems in small catchment hydrology for the past decade. These effects have not been addressed explicitly by most hydrograph separation studies. Thus, we do not know how *spatial* variations in end-member concentration affect the separation procedure. Harris *et al*. (1995) challenged the tracer community by arguing that traditional two-component hydrograph separations do not account explicitly for water and tracer mass balance because they fail to account for the volume that each component reservoir represents. Consequently, the main obstacle to evaluating these effects in natural catchments is our inability to close a tracer and water budget on an event timescale.

In natural experimental catchments, physical heterogeneity (in soil type, thickness, K_{sat}, topography, bedrock topography, etc.) confound our ability to constrain the water and tracer mass balance. Furthermore, given this imposed spatial variability in physical conditions, we cannot adequately sample all the possible geographic units in the catchment to assess the effect of pre-event water variability on flow separation estimates. This paper reports on a study of an artificial 490 m^2 catchment where we are able to close a water and tracer mass balance for a 120 mm storm at the site, and in so doing, address the following questions.

(1) Is the subsurface reservoir fully mixed?
(2) How do CHS and IHS of source components relate to volumes of water sampled for different catchment reservoirs?
(3) How are assumptions implicit in CHS and IHS violated, and what effect does this have on a computed f_e and f_{pe}?
(4) What is the linkage between the age, origin, and pathway of water flow in this catchment?

RATIONALE FOR USING AN ARTIFICIAL CATCHMENT

The Hydrohill catchment is perhaps the largest public works effort in small catchment hydrology in the history of mankind. The 490 m^2 grassland catchment took 100 workers 5 years to complete (Gu Weizu, personal. communication). The artificial catchment was designed to be intermediate between the complexities of natural watersheds and the idealities of soil columns. The large number of wells and lysimeters for sampling subsurface waters (described later) make this catchment a suitable location for testing mixing assumptions, closing a water and tracer mass budget, and linking process understanding to 'black box' source and flowpath separation studies. The catchment is 'real' or natural in the sense that it has intersecting slopes, a soil layer, and grass. However, it is artificial in that it was constructed with a homogeneous soil above a concrete aquiclude, a built-in drainage system comprised of stacked lysimeters, and impermeable retaining walls on all sides (Gu, 1988). The flow draining from different layers is separately funnelled through weirs at the bottom of the catchment, making accurate determination of water balances relatively simple. At this experimental catchment, we have the advantage of independent knowledge of spatial and temporal variation in the amounts and compositions of waters at different depths. Since Hydrohill drains rapidly after rainfall and generally no groundwater is present between storms (Gu and Freer, 1995), the pre-event component of the groundwater that develops DURING storms is derived from soil water recharged during the previous storms.

Samples collected from the artificial catchment were used to examine temporal and spatial heterogeneity of flowpaths and water compositions, to compare isotopes and different chemical species as tracers, and to illustrate the sensitivity of models to variability inside the 'black box'. In contrast to most other isotope hydrograph studies, at Hydrohill the dominant source of quickflow will be shown to be new water. This was true both at the beginning of the storm, when there was no groundwater, and late in the storm, when soils were saturated (Kendall, 1993). Large amounts of old water are stored in the silty loam soils of the unsaturated zone and are delivered (displaced and/or mixed with new water) to the saturated zone during storms by various combinations of macropore (bypass) and matrix flow (Kendall and Gu, 1992). Despite the fact that these ratios will be shown to be different from many investigations in forested catchments (as reviewed by Buttle, 1994), the results of this study are important in that they quantify the volumetric mixing of different soil layers and reservoirs.

DESCRIPTION OF THE STUDY AREA

The Hydrohill catchment was constructed for the purpose of studying rainfall-runoff processes in detail. The catchment is one of several instrumented catchments (Gu and Freer, 1995) located in the Chuzhou Hydrology Laboratory (the field experimental base of the Nanjing Research Institute of Hydrology and Water Resources), near Nanjing, China (118° 12′E, 32° 17′N). An entire hillslope was excavated to bedrock to create a bare catchment of 4573 m^2. Hydrohill, with a drainage area of 490 m^2, was later constructed within the bare catchment. A concrete aquiclude consisting of two intersecting slopes dipping towards each other at 10° with overall downslope gradients of 14° was created above the bedrock (Figure 1). Impermeable concrete walls enclose the catchment on all sides to prevent any flow of water between the bare and artificial catchments. Silt–loam soil that was removed from the site prior to excavation, was later slowly piled on the aquiclude to

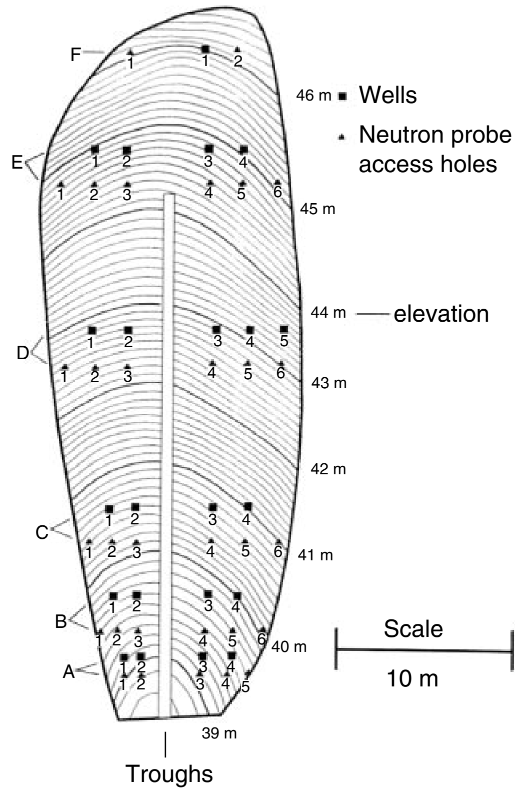

Figure 1. Plan view of the surface topography of the Hydrohill #2 experimental catchment showing the locations and numbers of wells and neutron probe access holes, and the central stacked lysimeter troughs. The numbers to the left of the map indicate the row number, e.g. well number 1 of row D is well D1, etc

a depth of about 1 m. Each soil layer removed during excavation was replaced during infilling at the same level. Hence, the final soil 'profile' was identical, at least in composition, to the natural soil cover. Also, the bulk density of the soil was adjusted during filling to approximate the natural soil profile before excavation. Grass was then planted over the surface. After allowing the soil settle for 3 years, a central drainage trench was constructed at the intersection of the two slopes and the water-sampling instrumentation was installed (Gu and Freer, 1995).

Five troughs, each 40 cm wide and 40 m long and constructed of fibreglass, were installed longitudinally in the trench. These troughs were stacked on top of each other to create a set of long zero-tension lysimeters (Figure 2). Each trough has a 20 cm aluminium lip that extends horizontally into the soil layer to prevent leakage between layers. Waters collected in the troughs are routed through V-notch weirs located in a gauging station under the hill where discharge is continuously monitored on strip chart recorders. Water samples are collected manually above the ponding at the weirs.

As illustrated in Figure 2, the uppermost trough collects rain; the next lower trough collects surface runoff. The next three troughs collect subsurface flow from soil layers spanning the depths of 0–30, 30–60, and 60–100 cm. These troughs will be referred to as the 30 cm, 60 cm, and 100 cm troughs. The source of the water in these troughs (i.e. whether the water is derived from interflow or saturated flow) varies locally and during storms. The lowermost trough collects either saturated flow or interflow, depending on the height of the water table. When the water table is high, saturated flow may be collected in both of the lower two troughs. The troughs are analogous to throughflow gutters located in hillslope pits in that water can only pour from the free face into the trough if there is a wedge of saturated soil extending upslope from the trough (Atkinson, 1978).

Two smaller pan lysimeters were installed at 1 m depth. Lysimeter 1 and lysimeter S are constructed of 4×8 m^2 and 1×2 m^2 sheets respectively, placed almost horizontally ($<5°$), that drain into the gauge house under the hill. Lysimeter S was located in the bare catchment adjacent to Hydrohill. A network of 21 access tubes for neutron moisture gages (Gu, 1987) and 22 wells for water-table measurements and water-sample collection were installed (Figure 1). The wells were drilled to the aquiclude and are slotted for the lowermost 20 cm. After installation of the wells, the spaces around the unslotted lengths of the pipes

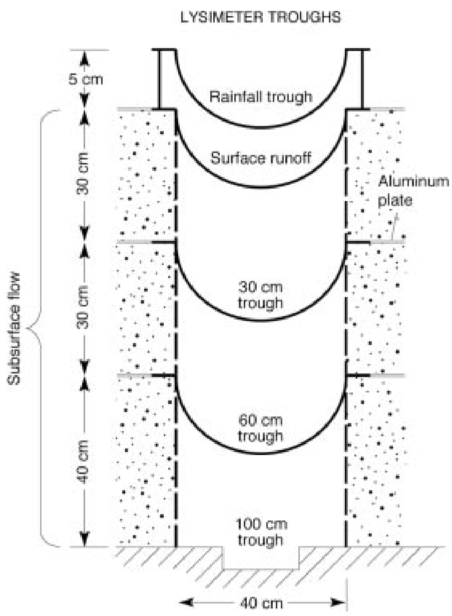

Figure 2. Schematic cross-section of rain, surface runoff, and subsurface flow collectors at the Hydrohill catchment

Table I. Soil properties[a]

Depth (cm)	Bulk density (g cm^3)	Porosity (%)	Grain size < 0·01 mm (%)	Organic matter (%)
0–30	1·44	45	48·66	0·87
30–50	1·42	46	45·33	0·63
50–75	1·40	48	45·32	1·05
75–100	1·60	39	37·33	0·40

[a] Average values from 12 profiles across the catchment.

were packed with clay to prevent vertical leakage along the outsides of the pipes. The neutron probe access holes were positioned adjacent to the wells and were numbered the same. An americium–beryllium neutron probe was used at depths of 30 and 60 cm to determine average moisture contents within a radius of about 25 cm. The uniform soil depths and relatively homogeneous soils (Table I) made calibration of the probe by conventional gravimetric methods very simple. Water contents of surficial samples (0–5 cm) were determined by conventional gravimetric methods and the values reported in volume percent water.

Rain amounts are continuously monitored using a standard WMO gauge located in the catchment, and samples are collected for analysis during storms. The average yearly rainfall is 950–1000 mm, and the average daily maximum temperature in July is 31·4 °C (Gu Weizu, personal. communication).

This artificial catchment drains rapidly and a laterally continuous water table develops only for large storms. Within hours after rainfall ceases, saturated conditions begin to disappear; hence, this catchment is more analogous to a hillslope than to an entire natural catchment with a perennial stream. Shrink–swell cracks can be seen at the surface and are similar in appearance to nearby natural undisturbed soils. Soil K_{sat} is in the range 5–20 mm h^{-1}; this will be shown later to be important for the production of infiltration excess overland flow.

METHODS

Two types of rain sample were collected simultaneously: sequential samples from the rain gauge and grab samples from the rain trough. Subsurface samples were also collected periodically from the troughs, and suites of groundwater samples were collected three times during the storm. The subsurface trough samples are more analogous to the rain trough samples than to the sequential rain samples, which contain the total rain collected over consecutive time periods.

Water samples were collected in 50 ml plastic bottles that were subsequently sealed with wax to prevent evaporation. Samples were analysed for oxygen isotopic composition ($\delta^{18}O$) at the US Geological Survey (USGS), Water Resources Division's stable isotope laboratory in Reston, Virginia, and for chemical composition at the USGS Panola Mountain Research Project laboratory in Atlanta, Georgia. Water was prepared for oxygen-isotope analysis by equilibration with carbon dioxide (Epstein and Mayeda, 1953). All isotopic compositions are expressed in permil relative to V-SMOW, with a 1σ precision of better than $\pm$0·05‰. Chloride (Cl) concentrations were determined using a 2120A Dionex[1] Ion Chromatograph, with 1σ precisions of $\pm$0·3 μeq l^{-1}. Silica (SiO_2) concentrations were measured with an autoanalyser with a 1σ precision of $\pm$0·8 μmol l^{-1}.

Determining accurate time-discharge relations was very difficult at Hydrohill because of problems the field workers had with the discharge recorders. Field engineers in China recorded stage values at changes in slopes on the hydrograph strip charts, made any necessary adjustments for recorder problems, and calculated discharge for each trough. The digitized sets of data were interpolated to determine values at 0·1 h intervals,

[1] Use of brand names in this report is for identification purposes only and does not indicate endorsement by the USGS.

and the higher-resolution digitized hydrographs were normalized to the records to convert stage values to discharge values. A number of small adjustments were then made to correct obvious timing problems. The times of samples collected during the storm starting on 5 July, 1989 are given in hours after 5 July, 00:00.

RESULTS

Water budgets

Over a 22 h period starting at 4 h on 5 July, two storm pulses produced 115 mm of rain at Hydrohill. 40 mm fell in the first 3 h of the storm. Low-intensity rain continued for about 10 h, and then the second pulse of high intensity rain continued at about 21 h (Figure 3). Antecedent wetness in the catchment prior to the event was low ($API_5 = 0{\cdot}3$ mm). The storm resulted in flow from the troughs starting at 6·7 h, after 20 mm of rainfall infiltrated on and into the soil (Figure 3) and produced saturation at the soil–aquiclude interface. In this report, we will use the term bedrock to refer to the concrete aquiclude and, hence, refer to this interface as the 'soil–bedrock' interface to enable the use of a now standard hydrologic term. Because no saturated zone existed prior to the event (as determined by checking the wells), subsurface flow in the troughs and wells is assumed to consist of various mixtures of pre-event soil water and event rain water.

The Hydrohill catchment is very responsive; the hydrographs of shallow interflow (30 and 60 cm) and saturated flow (100 cm) closely resemble the hydrograph of surface runoff (Figure 4). Time-to-peak for the 100 cm trough was 30–90 min later than for the 30 cm trough. However, because of timing problems noted above, detailed discussion of small differences in arrival times is probably not warranted. Small rainfall

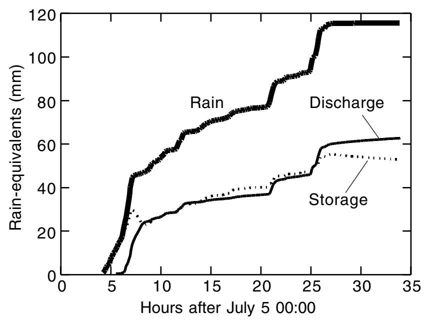

Figure 3. Cumulative rain, total discharge, and rain in storage; in millimeters (rain-equivalent millimeters)

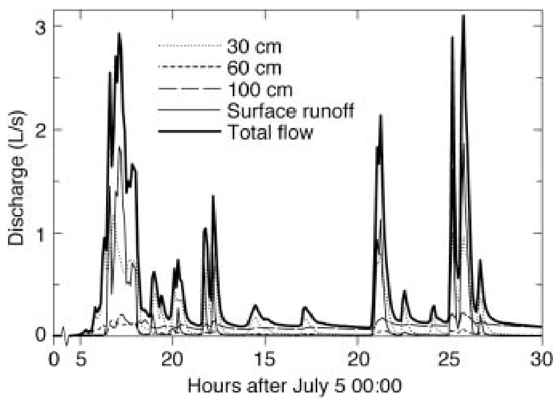

Figure 4. Discharge hydrographs for the 5 July, 1989 storm

amounts at 12 and 17 h caused discharge increases at 30 cm, 60 cm, and 100 cm, but not surface runoff. Hence, though rainfall intensity exceeded soil infiltration capacity during intense rainfall bursts, 1·7 mm h^{-1} rainfall during the period 13 to 17 h did infiltrate.

The maximum peak flow from the catchment during the two major rain pulses was about 3 l s^{-1}. About 50–80% of this flow was surface runoff, 30–40% interflow from 30 cm, <5% interflow from 60 cm, and 5–10% saturated flow from 100 cm (Figure 4). Whereas lateral soil water drainage occurred between pulses, 70–90% of the total discharge was saturated flow at the soil–bedrock interface from the 100 cm trough.

Groundwater levels were monitored frequently during the storm. Before the storm, the entire soil profile was unsaturated; saturated zones later developed unevenly (as mounds). The first well to become saturated was D3 (Figure 1), where the water table elevation rose to 40 cm by 7 h. The last well to saturate was B1, between 23 and 30 h. Hence, a laterally continuous water table did not develop until after 23 h and water levels continued to rise in most wells until about 30 h, when rained ceased. Water table elevations (above the aquiclude) ranged from 20 cm in the A and B wells on the left side of the trough to a large zone near the E and F wells where the elevations were in the range of 60–70 cm, with an average water table rise of about 35 cm. Subsurface samples were collected at 10, 17, and 34 h (Figures 6 and 7). Measurement of water table elevation changes (and sampling for isotopic and chemical analysis) allowed us to link geographic runoff sources in the catchment to time trends in trough flow at several times during the storm.

Moisture contents were measured several times during the storm in order to calculate changes in water stored in different horizons. Volume percent water contents of soils from 0–5 cm deep were determined gravimetrically (Table II) and water contents from 5–100 cm were determined by neutron probe (Gu Weizu, unpublished data) (Table III). The moisture contents suggest that about two-thirds of the available porosity (Table I) in the soils was filled with water once the catchment had wetted-up. Because the catchment soils became saturated unevenly and the neutron probe averages water contents over a large (25 cm) radius, the average moisture contents in Table III may hide a lot of spatial variability.

Table IV shows water budgets calculated for three overlapping periods of time when soil-water data were available. The periods all start at about 10:00 on 4 July (a day before the storm) and end at: 12 h (high flow during a shower); 20 h (at the end of a several-hour pause between the first and second pulses of rain); and 34 h (several hours after the end of the second rain pulse when the catchment was still draining). These three water budgets attempt to account for both the amounts of event rain water that have been added to different soil layers, and the amounts that have drained from these soil layers into the troughs. The water budget components are given in rain-equivalent units, i.e. scaled to the amount of rain in millimeters over an area of 490 m^2 required to account for INCREASES in the amounts of water present in or issued from each component of the catchment. Although the values for each component represent the increase in event water in

Table II. Moisture contents of surficial soils (determined gravimetrically)

Depth (cm)	Moisture content (vol. %)				Change in water content (%)		Rain-equivalent amounts (mm)	
	4 July	5 July			12 h[a]	20 h	12 h	20 h
		6 h	15 h	20 h				
0 to 1	22·5	60·4	64·5	58·7	+40·7	+36·2	+4·1	+3·6
1 to 2	22·5	36·3	64·5	58·7	+33·5	+36·2	+3·3	+3·6
2 to 5	22·5	36·3	40·2	46·7	+16·5	+24·2	+5·0[b]	+7·3
Total							+12·4	+14·5

[a] Values interpolated from 6 and 15 h data.
[b] The change in water content for the interval 2–5 cm has been multiplied by three.

Table III. Soil moisture contents (vol. %; determined by neutron probe)

Access tube #	4 July 09:30 (−14 h)		5 July 11:55 (12 h)		6 July 09:55 (34 h)	
	30 cm	60 cm	30 cm	60 cm	30 cm	60 cm
A2	28·3	31·3	32·1	32·5	32·2	32·3
C1	27·5	28·7	29·1	29·2	29·9	31·1
C6	28·0	29·7	29·6	30·6	30·2	31·3
D4	26·3	29·6	29·5	28·3	29·3	32·3
E2	30·3	33·6	30·2	32·8	32·4	33·5
E5	29·3	31·1	30·6	32·5	30·9	33·7
F2	27·6	31·2	30·7	32·7	31·3	34·2

Table IV. Event–water budgets from 4 July 10:00 to various times after 5 July 00:00[a]

Components	Rain-equivalent amounts (mm)		
	to 12 h	to 20 h	to 34 h
Surface runoff	13·1	14·0	23·5
Subsurface flow 0–30 cm	13·6	16·0	25·2
Subsurface flow 30–60 cm	0·8	1·1	1·7
Subsurface flow 60–100 cm	2·7	5·3	12·0
Soil water 0–5 cm	12·4	14·5	14·5[b]
Soil water 5–60 cm	17·1	17·7	18·3
Soil water 60–100 cm	5·1	7·5	9·9
TOTAL	**64·8**	**76·1**	**105·1**
Rainfall	61·4	76·7	115·5

[a] Although the agreements of inputs and outputs are excellent (e.g. 105%, 99%, and 91% for the three times), BALANCED water budgets are required for the subsequent isotope mass balance calculations [Equations (3) and (4)]. Discharges and rain amounts are easy to measure, so these values are probably accurate. Water contents, on the other hand, are more difficult to estimate, particularly when water contents are heterogeneously distributed; therefore, the errors probably are in these numbers. To eliminate the discrepancies in the water budgets above, −3·4, −0·6, and +10·4 mm of soil–water were added to the respective columns for later calculations of S_f amounts [Equation (4)].
[b] Estimated amount of water lost to evapotranspiration.

the catchment, the water actually measured in each component may be a mixture of event water plus pre-event water displaced out of the soil by the event water.

No gravimetric data for the surficial soils were available for 34 h, when the storm was over and the catchment was drying (Figure 3). Therefore, the amount of water present in the soils at 20 h, which reflects moisture conditions after several hours of draining and before much evaporation had taken place, is used as an estimate for the amount of water present at 34 h, a few hours after rain ceased at 29 h (Table IV). Given the low soil-water contents seen in the soils on 4 July, 3 days after a 7 mm storm that caused saturated flow (Table II), it is likely that much of the water once present in the shallow soils may have evaporated by 34 h. Hence, the water content given for the 0–5 cm component is probably a MINIMUM value for the amount of event water that was evaporated from the soil.

The neutron probe data for tubes A2, C1, D4, and F2 were used to determine the water contents of soils at various distances from the troughs. Measurements from the 30 cm and 60 cm probes were used as estimates for moisture conditions in the 5–60 cm and 60–100 cm intervals respectively. Based on several years of observations at all 21 access tubes, the moisture contents of these four tubes are believed adequate to characterize 17%, 10%, 40·6%, and 32·4% of the catchment, respectively (Gu Weizu, unpublished data). The volume percent changes in water contents for the four tubes are multiplied by these areal scaling factors to calculate the volume percent change in water content, which is then multiplied by the total depth of the interval for which the averages are being applied (i.e. 550 mm and 400 mm for the intervals 5–60 cm and 60–100 cm respectively) to calculate rain-equivalents in millimeters. The interception area of the catchment has been corrected for the area of the troughs (∼3%) because the rain water collected in the upper trough did not contribute to flow from the catchment.

There is excellent agreement between the calculated water budgets and rain amount at 12 h and 20 h (Table IV), with 105% and 99% respectively of the rain water accounted for in terms of discharge or increases in water content. The agreement for the last period (to 34 h), when the evaporative water loss in shallow soils could only be estimated and the deeper soils were contributing large amounts of discharge, is good, with about 91% of the rain accounted for in the catchment components.

The amounts of new water present in the 1 m soil zone at various times (Table IV) can be estimated by a slightly different method. Instead of using the neutron probe data to estimate water contents for the entire 60–100 cm zone, the average depths of the water table can be used to divide this interval into an unsaturated zone, where the neutron probe data can be used, and a saturated zone, where the water content can be estimated using the porosity. The available data were used to produce a contour map of water table elevations at 1063 evenly spaced nodes; these node values were averaged to produce the average elevations in Table V (Kendall, 1993). If the measured porosity of 39% (Table I) is used to calculate amounts of new water in the saturated zone, the total amounts of water stored in the soil (0–100 cm) for the three time intervals are about 50% higher than the values in Table IV (Kendall, 1993). Because the total water budgets in Table IV for 12 and 20 h are already in such good agreement with the rain input, the validity of these new estimates seems questionable. Possible explanations for the discrepancy are that pore spaces are much less uniformly and completely filled than estimated (i.e. less than the porosity of 39%), and that the saturated zone is much less continuous (Figure 5) than we assume for calculation purposes. If the maximum water content of 34% in Table III, which may be close to the maximum volume percent of water possible in the 5–100 cm soils under the kinds of saturated condition created in this catchment, is used instead to calculate the water contents in the saturated zone, the total calculated amounts of event water for the three time periods are 107%, 101%, and 92%. Because this is almost identical to the previous estimates, perhaps only 87% (34/39 × 100) of the total porosity in the deep soils can be saturated.

The amount of pre-storm soil water present in the catchment on 4 July is estimated to be 290 mm (using the measured water contents in Tables II and III). The maximum volume of water stored in the soil during the two storm pulses when soil data are not available can be estimated using the deep (5–100 cm) soil values at 34 h, when the deeper soils were thoroughly saturated and the 0–5 cm values observed at 14 h when surface runoff and 0–30 cm flow were near their maximum discharge values, to get 315 mm. Therefore, the

Table V. Average height of saturated zone and $\delta^{18}O$ of groundwater[a]

Hours after 5 July 00:00	Average height of water table (cm)	Average $\delta^{18}O$ of groundwater (‰)
10 h	8·8	−9·38
17 h	16·5	−8·57
34 h	35·5	−7·30

[a] Depths measured at 14, 17, and 33 h used for the calculations.

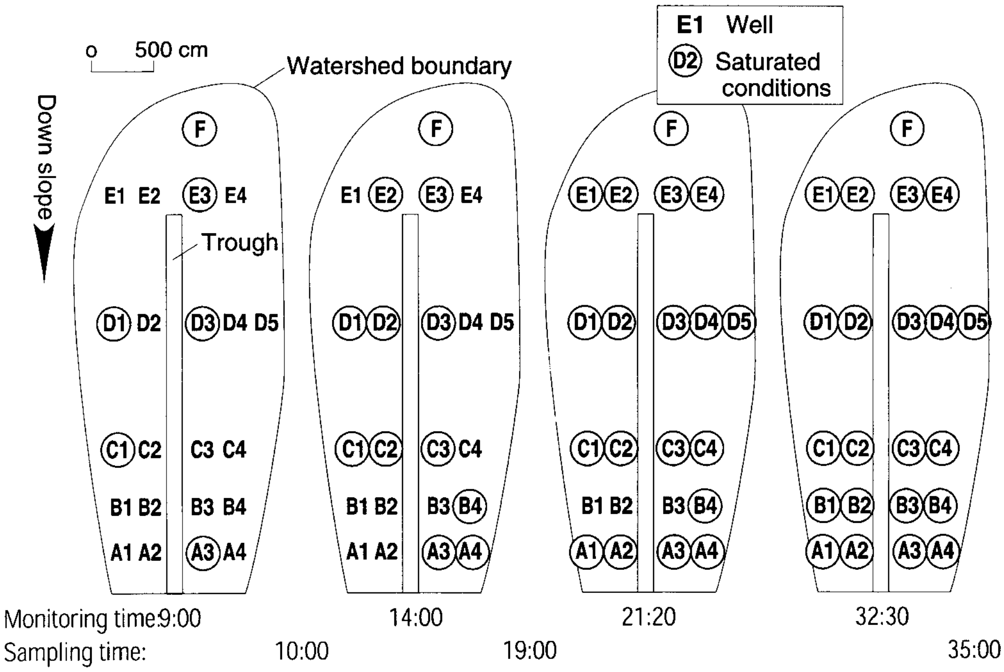

Figure 5. Four schematics of the catchment showing which wells had achieved saturation and four monitoring times (in hours after 5 July 00 : 00). The locations of the wells are indicated by letter–number pairs. Circled well numbers indicate saturated conditions at the wells at the monitoring time. Water collection times are indicated at the bottom of the figure. The $\delta^{18}O$ values of these well samples are shown in Figure 6. Modified from Kendall and Gu (1992)

pre-event water filled approximately 92% of total pore space eventually filled during the storm. If, under saturated conditions, the pore spaces in the interval 5–100 cm can contain 34 vol.% water, the maximum possible storage for the 1 m soil zone is 357 mm.

Isotopic compositions

The volume-weighted $\delta^{18}O$ of the rain storm was −11·3‰. The isotopic composition of the 14 sequential samples of rain collected gradually decreased from an initial −8·3‰ to −12·5‰ during peak rainfall, and then increased to −9·65‰ at the end of the storm. The 14 'grab' samples collected from the rain trough showed almost identical variability; for clarity, the $\delta^{18}O$ values of the rain trough samples are plotted in place of the sequential rain samples in Figure 6b.

A few samples of pre-event waters were available. A complete set of soil samples had been collected to characterize the pre-event soil water; unfortunately, the centrifuge method used to extract the water caused isotopic fractionation of the samples, so they will not be discussed further. The 7 mm hour-long storm on 1 July caused a small quantity of surface runoff with a $\delta^{18}O$ value of −8·35‰ and a minute amount of saturated flow from the 100 cm trough with a composition of −5·45‰. The surface runoff $\delta^{18}O$ value is probably representative of the composition of the 1 July rain storm, and the fact that measurable runoff occurred from such a small storm probably indicates that the surface soils were saturated at this time. From 2 July until the storm on 5 July, the wells were dry, the catchment yielded no subsurface flow, and the catchment soils became progressively dryer. Saturated flow from a large storm on 25 June had a $\delta^{18}O$ value of −5·85‰.

One way of estimating the composition of pre-event water that takes into account possible intrastorm changes in the composition of pre-event water is to average the compositions of baseflow prior to the storm

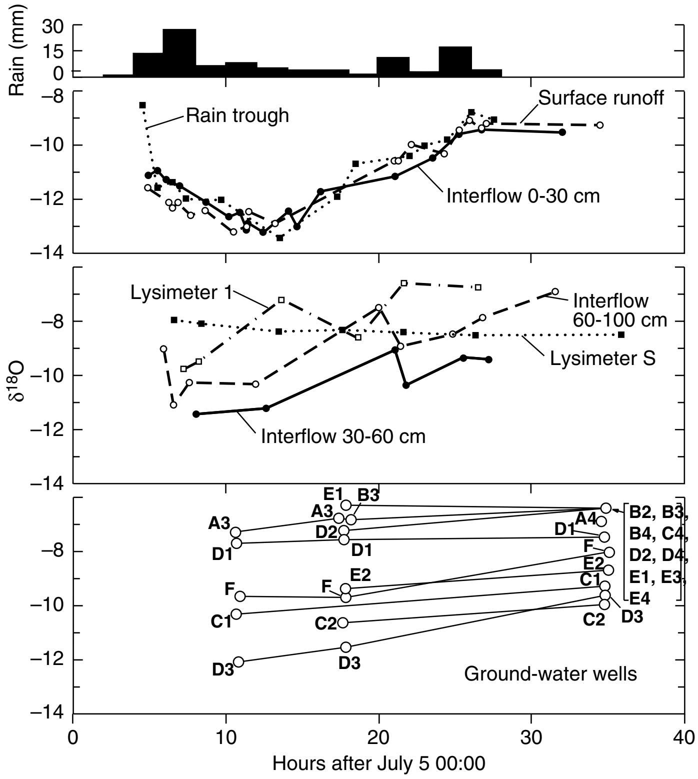

Figure 6. (a) Amounts of rain collected at the rain gauge at 2 h intervals; (b) $\delta^{18}O$ values of rain, surface runoff, and 30 cm interflow; (c) $\delta^{18}O$ values of 60 cm interflow, 100 cm saturated flow, and lysimeter samples; (d) $\delta^{18}O$ values of groundwater. Data points are connected with lines to clarify the different isotopic patterns; error bars are smaller than the symbols

and during hydrograph recession (Hooper and Shoemaker, 1986). The last sample of saturated flow at 31·5 h had a composition of −6·85‰ (Figure 6c); the average of this and the pre-event flow from 1 July gives −6·15‰. On the basis of these limited data, the soil water prior to the 5 July storm was enriched in ^{18}O relative to the rain water, in the range of −5·5 to −8‰. This estimation ignores the possible isotopic enrichment of very shallow soil water caused by evaporation between 1 July and 5 July because: (1) any such waters are volumetrically insignificant compared with the total water storage; and (2) exchange of the evaporated waters with atmospheric water plus contributions of water from dew can cause these shallow soil waters to have a lower $\delta^{18}O$ than expected (Vance C. Kennedy, unpublished data).

The $\delta^{18}O$ values of samples collected from the three subsurface flow troughs and the two pan lysimeters provide information on the mixing of rain and pre-storm waters, and on the timing of mixing, as infiltration waters arrive at different soil horizons. Although all the hydrographs are similar (Figure 4), the isotopic compositions of waters collected in the five troughs have two different patterns as shown in Figure 6b and c. The rain, surface runoff, and interflow from 30 cm all have very similar $\delta^{18}O$ values during the storm (Figure 6b). The $\delta^{18}O$ values of water from 60 cm and 100 cm (Figure 6c) show no similarities to the shallower samples. The temporal changes in $\delta^{18}O$ of 60 cm and 100 cm samples are similar, although the deeper samples have $\delta^{18}O$ values that are 1 to 2‰ higher. Samples from lysimeter 1 show a similar pattern, but with different lag times. Lysimeter S has an almost constant isotopic composition, indicative of pre-event water, perhaps because of drainage problems.

Samples from below 30 cm seem to show a correlation between discharge and isotopic composition. As discharge decreases from 10 to 20 h, the 60 cm and 100 cm samples show gradually increasing $\delta^{18}O$ values.

An increase in discharge caused by increased rain intensity at 21 h is associated with lower δ^{18}O values, and then δ^{18}O values increase again as the soils drain. The final waters flowing at the 30 cm and 60 cm interflow troughs are almost identical in δ^{18}O to the last rain samples. Water continues to flow at the 100 cm trough for several hours past the end of the rain, and the δ^{18}O values of the saturated-zone water continue to increase towards the original composition of pre-storm water. Lysimeter 1 samples also increase in δ^{18}O as discharge decreases after the first rain pulse, but then show a sudden decrease in composition about 4 h before the other deep samples. At the end of the storm, the lysimeter waters have high δ^{18}O values similar to those seen in the isotopically enriched wells (Figure 6d). Lysimeter S samples show much less variation than the other collectors and actually decrease slightly in isotopic composition over the storm, unlike the rest of the sampling sites.

The groundwater in this tiny catchment shows considerable spatial and temporal variability in δ^{18}O, with values ranging from -12 to -6‰ (Figure 7). Wells can also be divided into two categories by their isotopic responses to the storm (Figure 6d): (1) wells where the initial waters have high δ^{18}O values ($-6{\cdot}5$ to $-7{\cdot}5$‰) and remain approximately constant during the storm; (2) wells where the initial δ^{18}O values are considerably lower (-10 to -12‰) and become 1 to 3‰ higher (i.e. enriched in ^{18}O) during the storm. The changes in the δ^{18}O values of groundwater are not erratic, but instead reflect ongoing processes affecting sizable portions of the catchment during the entire storm. At 10 h, waters with low δ^{18}O values (<-10‰) are found in two areas located on either side of the central troughs (Figure 7). Groundwater in these two areas has a δ^{18}O value lower than the rest of the catchment throughout the storm, although the values gradually become higher at 20 and 34 h as the water table rises. Groundwater elsewhere also becomes slightly more enriched in ^{18}O from 10 to 34 h; areas that were most enriched in ^{18}O at 10 h are still enriched relative to most wells at 34 h.

There is no consistent relation between changes in water table level and changes in δ^{18}O (Figures 5–7). Although the waters with low δ^{18}O values at D4 are associated with transient groundwater mounds, the other zone with low δ^{18}O values located near C2 is associated with a steadily rising water level. The zones where waters are most enriched in ^{18}O include areas where the water table rose rapidly (E and F wells) and areas

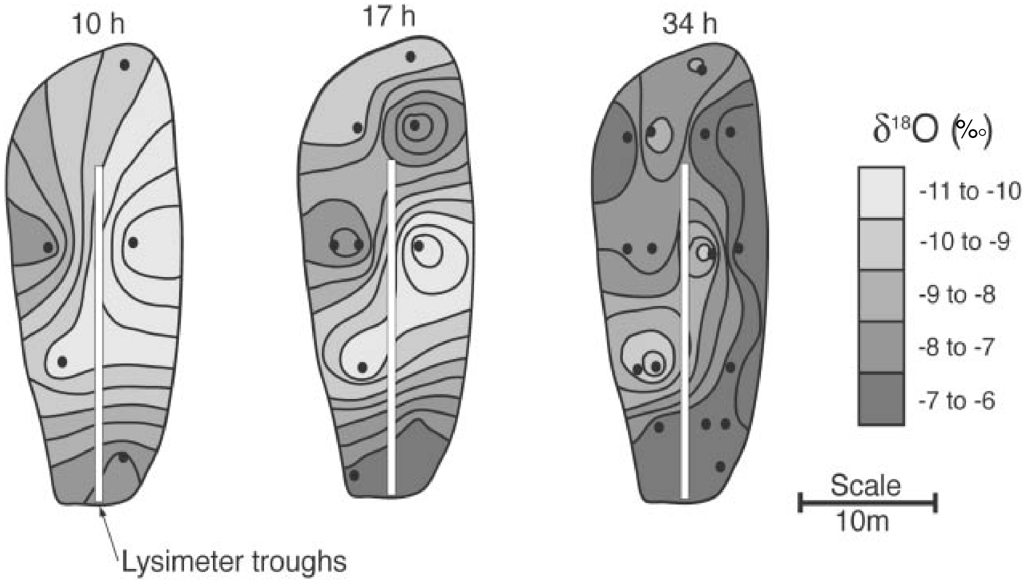

Figure 7. Cartoons showing estimated δ^{18}O in groundwater at three sampling times. The solid dots indicate the locations of wells where δ^{18}O values were available at these selected times. Considerable poetic licence is required for contouring so few data, especially across the central axis where the troughs divide the catchment. However, the coherency of the spatial and temporal patterns provides some validation of this approach as a useful exercise

where the water table never rose very high (A and B wells). At the end of the storm, the groundwaters in the middle part of the catchment, near the trough, appear to contain the highest amounts of event water (Figure 7).

Chemical variability

Concentrations of Cl in rain collected in the rain gauge were two to three times higher than in rain samples collected in the rain trough; this may be a consequence of using poorly rinsed collection bottles in the rain gauge. Therefore, the rain trough samples were used for estimating the composition of 'new' water. Although the high concentration of the first sample may be partially due to dissolution of salt deposits in the rain trough, in addition to atmospheric washout, the volume-weighted Cl and SiO_2 concentrations of rain are 7 μeq l^{-1} and 8 μmol l^{-1}, respectively. Concentrations of Cl and SiO_2 are low in surface runoff, which is sometimes almost as dilute as rain, and high in subsurface flow (Figure 8a and b), with an average of about 30 μeq l^{-1} for Cl and 200 μmol l^{-1} for SiO_2. Concentrations of SiO_2 in surface runoff are similar to those of subsurface samples only at times of high rain intensity and peak flow; the high concentrations at this time may result from return flow through the upper soil layers.

Groundwater samples did not have consistent chemical compositions (Figure 9a); in fact, they showed considerably more variation in Cl and SiO_2 concentrations than was seen in the trough samples. The Cl and SiO_2 data weakly support the observation made with $\delta^{18}O$ that the groundwater wells can be divided into two categories. The wells with constant but high $\delta^{18}O$ values have a wide range of Cl values, but the changes in Cl over time for any individual well are small and erratic and there is no correlation between changes in $\delta^{18}O$ and in Cl. In contrast, all the wells that initially had low $\delta^{18}O$ values but which became more enriched in ^{18}O during the storm also showed a strong inverse relation between Cl and $\delta^{18}O$ (Figure 9b).

Hydrograph separation

The amount of rain water contributing to subsurface flow at any sampling time can theoretically be calculated using simple conservative-mixing models, although such complex subsurface flow hydrographs (Figure 4) really require more frequent samples than are available. In the simplest application of the IHS technique, one assumes that all subsurface water results from mixing of only two components, event and pre-event water,

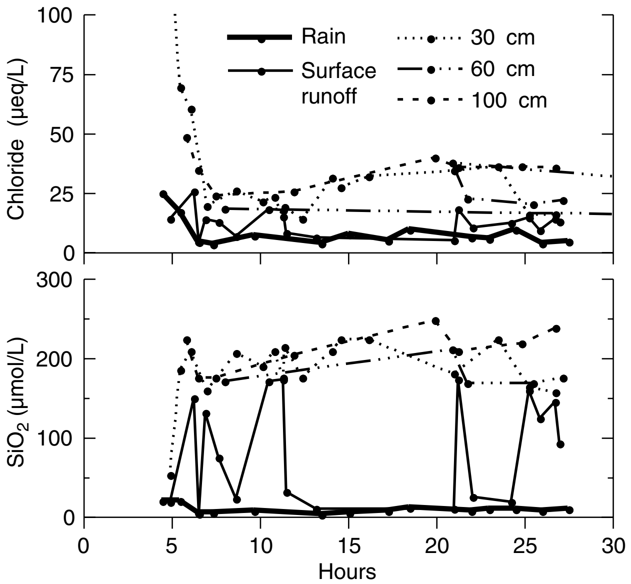

Figure 8. Chloride (a), and silica (b) concentrations in trough samples. Data points are connected with lines to clarify the different patterns

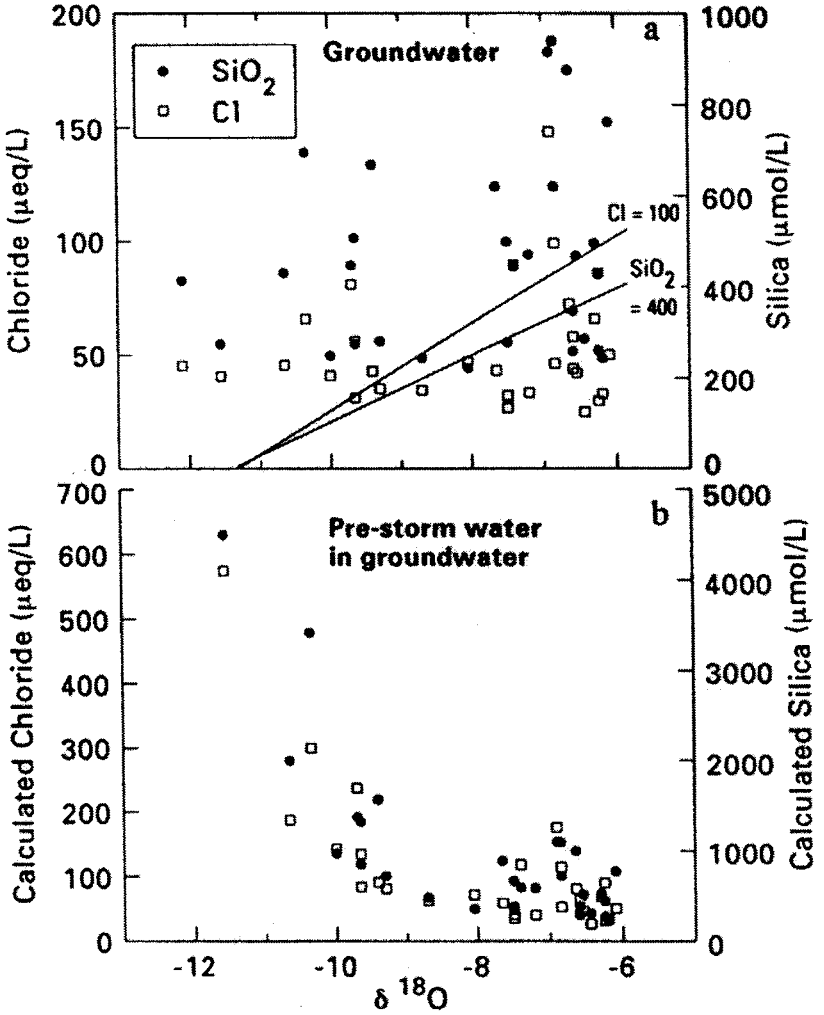

Figure 9. (a) Measured values for chloride, silica, and $\delta^{18}O$ in groundwater samples. The solid lines are mixing lines showing the calculated concentrations of chloride and silica in groundwater that would be produced from conservative mixing of pre-event waters (Cl = 100 μeq l^{-1}, SiO_2 = 400 μmol l^{-1} and $\delta^{18}O = -6‰$), with event waters (Cl $\approx$ 0, $SiO_2 \approx 0$, and $\delta^{18}O = -11{\cdot}4‰$). (b) Calculated chloride and silica concentrations of *pre-event water* in groundwater, assuming that the amounts of pre-event water calculated using $\delta^{18}O$ (using cumulative rain) are accurate. Error bars are smaller than symbols

both having spatially and temporally constant $\delta^{18}O$ compositions. For these calculations, a number of other assumptions must be made about the water sources.

For isotope and chemical separations, the choice of end-member compositions (i.e. the compositions of event and pre-event water) is critical. As discussed earlier, the meagre pre-event data suggest that the $\delta^{18}O$ value of this water was likely in the range of $-5{\cdot}5$ to $-8‰$. A $\delta^{18}O$ value of $-6 \pm 1‰$ was chosen for pre-event water because: (1) the various reasonable proxies for pre-event water discussed earlier all had $\delta^{18}O$ values near $-6‰$; (2) samples from lysimeter 1, the 100 cm trough, and groundwater wells seemed to 'trend' towards this value at the end of the storm; (3) there was insufficient information to assign a spatially variable composition to the soil water. If a more typical value of -7 or $-8‰$ is used, the calculated percent of event water contributing to subsurface waters exceeds 100% for many sampling times, indicating that the isotopic compositions of these subsurface waters are not intermediate in composition between the two proposed end-member compositions. Other possibilities that cannot be ruled out include: that the true unsaturated-zone water $\delta^{18}O$ value could be even higher than −6‰, that it could be vertically or horizontally stratified, or that the soil-water could be heterogeneous in composition because of poor mixing of waters from the previous storm (e.g. the pre-event water could show spatial variability similar to Figure 7). These different proxies for pre-event water also had relatively constant Cl and SiO_2 values, which were used for the chemical end-members.

Three possible approaches for estimating the event-water component are: (1) the conventional approach (Sklash and Farvolden, 1982), which uses the bulk composition of rain for the event-water component; (2) use of the actual, sequential rain value at the time each subsurface sample is collected (with or without a lag time); (3) use of the cumulative volume-weighted average of all the rain preceding each sampling time. Because of the large range of rain compositions during the storm and the existence of these same isotopic variations in the subsurface waters at 30 cm, use of the bulk rain composition is inappropriate. The two latter approaches often produce significant differences in the percentages calculated for different water sources (McDonnell *et al.*, 1990), as illustrated in Figure 10. Generally, this plot shows that, when subsurface flow is high, the contribution of event water is high; otherwise, as the soils drain, the contributions of pre-storm water increase. Not surprisingly, there appears to be more event water present on the rising than on the falling limbs of each discharge peak. During flow peaks, the amount of event water ranges from 50 to 95% of the subsurface flow; between peaks, the flow may contain only 20–60% rain. The longer the draining time between discharge peaks, the less rain water present in the subsequent discharge peaks.

During the first part of the storm until the increase of rain intensity at 21 h, use of cumulative rain values produces higher (by 5–20%) estimates of the amount of subsurface water derived from this storm than use of sequential rain compositions. After this time, the cumulative rain values produce markedly lower estimates of rain contributions than the sequential rain values. This change, shown by a 'cross-over' at 15 h in Figure 10, occurs during a period of low rainfall intensity (Figure 6a). The wells with water consistently enriched in ^{18}O (Figure 6d) contained only 10–20% rain water at 10 h, decreasing to generally less than 5% rain water at 34 h; essentially the same percentages are calculated regardless of whether the sequential or the cumulative rain value is used. Because these wells contain virtually no event water, the infiltration of event water at the surface must be displacing pre-storm isotopically enriched soil water downwards to create local saturated conditions above the soil–bedrock interphase. The wells that show increases in $\delta^{18}O$ with time initially (10 h) yielded

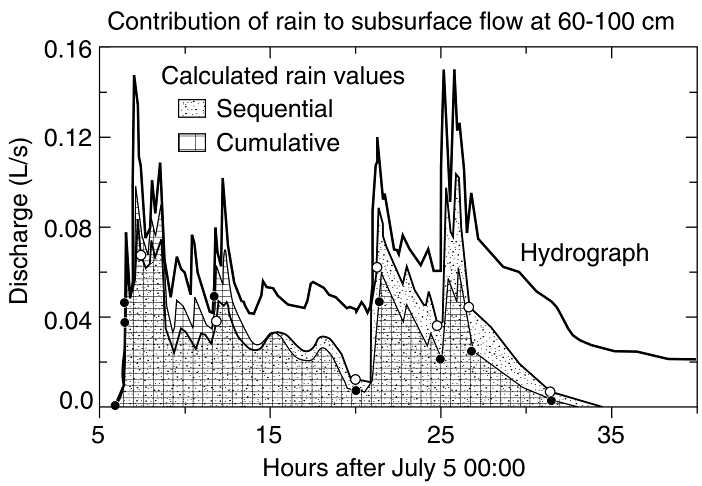

Figure 10. Estimates of the percentage of subsurface flow at the 100 cm collector that is derived from rain, calculated using soil water of −6·5‰, and using both the sequential rain values (dots) and the volume-weighted cumulative values (circles). The shaded areas represent the amount of total discharge derived from rain

groundwater containing 50–100% event water; by 34 h, many of these wells contained only 20–50% event water. The waters in these wells are apparently mixtures of rapidly moving low-$\delta^{18}O$ rain water travelling through macropores with increasing amounts of pre-event water with higher $\delta^{18}O$ values flowing downwards by matrix flow.

DISCUSSION

Comparison of information provided by different hydrograph separation methods

This study advocates that applying multiple black box models is useful for hydrograph separation and constraining one's understanding of storm catchment response. For example, hydrologic, chemical, and isotopic models can provide information about catchment responses, flowpaths/residence times, and water sources respectively. All three types of hydrograph separation model are applied to the 5 July storm. Separations were made for surface runoff, 30 cm subsurface flow, 100 cm subsurface flow, and total flow from the catchment. The end-member values chosen for the IHS and CHS models are given in Table VI. Hydrologic data for the 60 cm trough were not modelled separately because the flow was insignificant (3% of total) compared with the other troughs (Figure 4) and because of some peak-timing problems. Details of the instantaneous unit hydrograph (IUH) calculations can be found in Kendall (1993) and Hansen *et al.* (1997).

The IUH models for surface runoff and 30 cm subsurface flow (Table VII) indicate that the discharge from these zones is about 100% quickflow. The model fits have r^2 values of 0·89 and 0·90 respectively, showing that the hydrologic responses were strongly linear (Hansen *et al.*, 1997). As expected, comparison with the $\delta^{18}O$ separations shows that the quickflow here is composed entirely of event water (98–112%). The Cl and SiO_2 separations for these troughs suggest much more pre-event water (20–65%) than seen with $\delta^{18}O$. The percentages of new water calculated by each tracer are approximately constant at 12, 20, and 32 h (Table VII).

The IUH model for the 100 cm trough fits the actual discharge data with an r^2 of 0·87 (Hansen *et al.*, 1997), and indicates that most (78–84%) of the flow is slowflow, except at discharge peaks where the amount of quickflow can approach 50%. Clearly, the correlations between quickflow and event water—and slowflow and pre-event water—seen in shallow samples are breaking down at depth. Although the $\delta^{18}O$ values suggest that as much as 50% of the water collected in the 100 cm trough as the soils drain is event water, by the RESPONSE CHARACTERISTICS, almost all this water appears to be slowflow. A reasonable conclusion from this is that waters from different sources are behaving hydrologically the same and hence have become well-mixed.

The total-flow hydrograph is analogous to what might have been collected from a deeply incised stream within the catchment. The IUH model indicates that 77% of the flow is quickflow and 23% is slowflow at 32 h. The $\delta^{18}O$ separation gives about 12% pre-event water and the chemical separations about 45–55% pre-event water. These percentages are unusual; in most catchments studied to date, the quickflow is predominantly derived from old water.

It is interesting that the two chemical separations are so similar to each other for the various troughs (Table VII). In the absence of contradictory $\delta^{18}O$ data, the similarity of Cl and SiO_2 separations could have been used as confirmation that the solutes were behaving conservatively. On the contrary, the IUH and IHS

Table VI. End-member compositions chosen for hydrograph separation models

End-member	$\delta^{18}O$ (‰)	Chloride (μeq l^{-1})	Silica (μmol l^{-1})
Event water	sequential rain samples	7	8
Pre-event water	−6	40	275

Table VII. Calculated cumulative amounts of event water and quickflow for the hydrograph separation models using $\delta^{18}O$, silica, and chloride[a]

Trough	12 h				20 h				32 h			
	Event (%)			Quick (%)	Event (%)			Quick (%)	Event (%)			Quick (%)
	$\delta^{18}O$	SiO_2	Cl		$\delta^{18}O$	SiO_2	Cl		$\delta^{18}O$	SiO_2	Cl	
Surface runoff	112	70	79	100	106	72	80	100	98	65	80	100
Runoff												
30 cm	107	35	43	100	103	34	45	100	100	36	45	100
60 cm	95	80	97	—	84	67	80	—	77	68	71	—
100 cm	77	33	42	22	61	26	32	16	52	20	22	16
total flow	102	51	60	89	95	48	58	78	88	45	55	77

[a] The percent quickflow values were calculated using four different IUH models (Hansen *et al.*, 1997), one for each trough; hence, the values are not additive.

model results support the hypothesis that the event quickflow is picking up sizable amounts of Cl and SiO_2 during rapid, very surficial, contact with the soil before being collected as surface runoff and 30 cm interflow. The additional solutes could be derived from less-mobile pore waters with concentrations higher than that estimated for pre-event water, which is reasonable in surficial soils subject to evaporative concentration, or by desorption (Kennedy, 1971; Kennedy *et al.*, 1986). However, these waters were not successfully sampled in this study.

It has been shown that some chemical tracers can provide an estimate of the amount of flow derived from overland or shallow subsurface stormflow because the limited contact time with the soil should permit little alteration of the chemical content of rain (Elsenbeer *et al.*, 1995); this premise is not valid at Hydrohill. The Cl and SiO_2 concentrations in rapid-flowing surface runoff and 30 cm interflow are two to ten times the concentrations seen in rain. This very rapid uptake of solutes would tend to cause underestimation of the amounts of streamflow derived from shallow flowpaths and event water sources calculated using chemical tracers.

The close match of the separations estimated using the two chemical tracers, in this study and in previous studies, may be largely fortuitous. In this catchment, there was no baseflow and other indicators of pre-event water had to be used. Other choices could have been made for pre-event water for the calculations in Table VII (i.e. instead of the values in Table VI), resulting in different percentages of event and pre-event water (McDonnell *et al.*, 1991). For example, inspection of the groundwater data (Figure 9a) suggests that two types of pre-event soil water might be present in the catchment: a more mobile water (i.e. one with a variable $\delta^{18}O$ value, characteristic of event-derived waters) with a Cl composition of 30–40 $\mu eq\ l^{-1}$ and a less mobile water (i.e. one with the $\delta^{18}O$ value of pre-event water, $-6‰$) with a Cl concentration of $\sim 100\ \mu eq\ l^{-1}$. Using a value of $100\ \mu eq\ l^{-1}$ results in about twice as much event water in total flow as was calculated for Table VII (using the $Cl = 40\ \mu eq\ l^{-1}$). Slow-moving water (i.e. with $\delta^{18}O = -6‰$) appears to have a SiO_2 concentration of about $400\ \mu mol\ l^{-1}$; use of this value instead of the value of $275\ \mu mol\ l^{-1}$ typical of fast-moving water (Tables VI and VII) produces about 50% more event water in total flow. If concentrations of $100\ \mu eq\ l^{-1}$ and $400\ \mu mol\ l^{-1}$ had been chosen for Cl and SiO_2 respectively for the calculations that produced Table VII, the two chemical hydrograph separations would not have agreed and one or both solutes would have been considered to be behaving nonconservatively.

In theory, these same concentrations can also be used to estimate the percent of event water in groundwater. Although neither choice for SiO_2 (i.e. 275 or $400\ \mu mol\ l^{-1}$) is satisfactory for such calculations because the groundwater is generally more saline than either, the value of $Cl = 100\ \mu eq\ l^{-1}$ for the pre-event concentrations of Cl appears moderately satisfactory. If Cl and SiO_2 were behaving conservatively, there should be linear relations between the $\delta^{18}O$ and solute compositions of groundwater. Thus, the amounts of event and pre-event water determined using $\delta^{18}O$ values can be used to calculate what the Cl and SiO_2 concentrations in groundwater *should* be if the solutes were conservative tracers of event *versus* pre-event water; these theoretical linear relations for groundwater are shown as lines in Figure 9a. It is clear that there is no correlation of the actual and these theoretical values; the chemical compositions of pre-event water in zones that deliver water to the troughs are apparently different than the compositions in zones that are sampled by the wells.

So what were the solute concentrations of pre-event water in the pore-waters that were displaced by event rain to become groundwater? These concentrations can be estimated using the percentages of event water calculated with $\delta^{18}O$ (using cumulative rain), to produce the data in Figure 9b. The wells that contained high and approximately constant amounts of pre-event water throughout the storm (i.e. wells with high $\delta^{18}O$ values) had pre-event water of a relatively constant chemical composition of $Cl = 100$ μeq l^{-1} and $SiO_2 = 1000$ μmol l^{-1}. The wells with $\delta^{18}O$ values that increased during the storm (i.e. had increasing amounts of pre-event water), show a negative correlation between chemical concentration of pre-event water and the amount of pre-event water. The more 'old' water there was in these wells, the lower the solute concentration in the original pre-event water mixing with the rain water. The calculated pre-storm Cl and SiO_2 concentrations were highly correlated ($r^2 = 0{\cdot}89$). The apparent higher salinities of the pre-event waters in wells with higher concentrations of event water (i.e. $\delta^{18}O < -9‰$) could be explained by some initial flushing of salts from the walls of macropores by early infiltrating rain water. Alternatively, the pore-waters that are displaced early in the storm by rain water are more saline than the ones displaced later. In either case, the solutes are definitely not behaving conservatively. The existence of macropores is supported by the common soil fissures, the rapid hydrologic response, and the development of transitory hydrologic mounds at the aquiclude (Kendall and Gu, 1992; Kendall, 1993; Gu and Freer, 1995).

In this catchment, we have independent knowledge of the amounts of water flowing as surface and subsurface flow (Table IV) and can compare these amounts with estimates calculated with the chemical hydrograph separation models (Table VII). For the TOTAL discharge up to 32 h (34 h), 38% of the discharge (23·5 mm/62·4 × 100) is surface runoff and 62% is subsurface flow from the three subsurface troughs. Based on the CHS calculations in Table VII, the surface runoff is dominated by event water and subsurface flow is dominated by pre-event water. The amount of event water (as determined by the chemistry) in the total flow from the catchment, which should be equivalent to the amount of surface runoff (Wels *et al.*, 1991), ranges from 36 to 45% for calculations made with SiO_2 and Cl; these values are in excellent agreement with the discharge measurements.

However, closer inspection of the percentages of event water collected in the different troughs shows that there is a problem with this apparent agreement: 20 to 35% of the surface runoff, which should be all event water based on the chemistry (because of the shallow flowpath), is apparently pre-event (based on the chemistry, or 'chemically' pre-event). And about 35% of the subsurface flow that should be all pre-event water (because of the deeper flowpaths) is 'chemically' event water. Therefore, the agreement between the actual amounts of discharge collected from surface runoff and subsurface flow, and the total amounts calculated by the chemical separations appears to be largely FORTUITOUS. Hence, these chemical tracers do not give accurate estimates of the amounts of water flowing along different pathways at Hydrohill. The differences in the amounts of event water calculated using $\delta^{18}O$ and solutes suggest that the chemically pre-event water component of surface runoff is probably an artifact of the high salinity of surficial pore-water and/or dissolution of surficial salts. Comparison of the four separations for 100 cm flow (Table VII) suggests that a part of the event-water component of subsurface flow is probably a result of large amounts of dilute rain water flowing in macropores and responding as subsurface stormflow.

Isotope mass balances

About 98 ± 7% of the event rain inputs to the catchment at 12, 20, and 34 h (Table IV) can be accounted for in increases in soil moisture contents or discharge. These water mass balance agreements are generally good enough for isotope mass balance calculations to be considered feasible. To fine-tune these water budgets, the water mass balance is formulated below in terms of the TOTAL amounts of water present in the system, instead of accounting for just the new water, as was done for Table IV:

$$R + S_i = Q + S_f \tag{3}$$

where the inputs are: R is the rain and S_i is the initial amount of pre-storm soil-water stored in the catchment; and the outputs are: Q is the total discharge and S_f is the final amount of pore water stored in the catchment at the times the calculations were made. The water budget equation (Equation (3)) does not include a term for evaporative loss because the calculations for 0–5 cm water in Table IV already included estimates, probably underestimates, of the amounts of water that had been present in the system prior to evaporation. This formulation improves the water mass balances calculated in Table IV (see caption for details); the water outputs are 101%, 100%, and 97% of the water inputs for the three calculation times used.

The isotopic composition of water left in pore spaces in the catchment (Table VIII) can be calculated from these data using an isotope mass balance equation:

$$R\delta_R + S_i\delta_{Si} = Q\delta_Q + S_f\delta_{Sf} \tag{4}$$

where δ_{Si} and δ_{Sf} are the initial and final $\delta^{18}O$ values of the stored soil pore-water. The $\delta^{18}O$ values of flow at 32 h were extrapolated to 34 h for these calculations because few samples were collected at 34 h. The $\delta^{18}O$ of pre-event water was assumed to be -6 ± 1‰; use of values outside this range resulted in mass balance problems. The total (net) flow was calculated by summing up the 0·1 h interval interpolated discharges for each of the collectors (Hansen *et al.*, 1997). The net $\delta^{18}O$ of total flow was calculated by multiplying the 0·1 h interpolated $\delta^{18}O$ values by the discharges from each of the collectors, and dividing by the net discharge. Cumulative $\delta^{18}O$ values (as per McDonnell *et al.* (1990)) were used instead of sequential values because the soil storage is expected to be much less 'flashy' than subsurface flow to the troughs, which is mainly transported *via* bypass flow. Because much of the rain from the first rain pulse might have already drained from the soils before rain started again at 21 h, the calculations at 32 h were made using both the total cumulative $\delta^{18}O$ value at 32 h (−11·3‰) and the cumulative $\delta^{18}O$ value for only rain between 20 and 34 h (−10·2‰).

Several other assumptions were made: (1) the amount of water fractionated by evaporation was negligible compared with the amount of water stored in the soil (290 mm before the storm); (2) event water was

Table VIII. Isotope mass balance calculations[a]

Components	$\delta^{18}O$ (‰)		
	12 h	20 h	34 h[a]
Cumulative rain (δ_R)	−11·6	−11·9	−10·8 ± 0·6
Surface runoff	−12·3	−12·3	−11·2
0–30 cm interflow	−12·0	−12·1	−11·4
30–60 cm interflow	−11·4	−11·0	−10·1
60–100 cm saturated flow	−10·4	−9·7	−8·8
Total flow (δ_Q)	−11·8	−11·6	−10·7
Soil water (δ_{Sf})	−6·6 ± 0·9	−6·8 ± 0·9	−6·8 ± 0·9
Water in catchment storages			
Event rain stored in catchment (%)	53·8 ± 0·1	57 ± 2	52 ± 10
Original pre-event water stored in catchment (%)	100 ± 1	99 ± 1	97 ± 3

[a] Isotopic compositions at 32 h used in the calculations because none available at 34 h. Two estimates of cumulative rain $\delta^{18}O$ used.

well mixed in the catchment; (3) prior to the storm, the soils were homogeneous in isotopic composition ($\pm 1‰$), with mobile waters identical in $\delta^{18}O$ to immobile waters. The error bars noted in Table VIII indicate the possible spread of values calculated using the range of possible compositions discussed above. The uncertainties are greater for longer time periods because of the range of reasonable estimates for rain $\delta^{18}O$, and because water mass-balance problems become larger later in the storm when evaporative losses are more difficult to estimate.

There is some evidence of preferential storage of different time-fractions of the storm, in violation of the above assumptions. For example, the 0·2‰ lower $\delta^{18}O$ value of total flow relative to rain at 12 h (Table VIII) is probably an example of small-scale preferential storage. Instead of rain being well mixed in the catchment, a portion of the early ^{18}O-enriched rain ($-8{\cdot}4‰$) was probably preferentially retained in the shallow dry soils. This conclusion is supported by the lower $\delta^{18}O$ values of total surface runoff and 30 cm interflow relative to total rain. The lower values also indicate that either there has been little or no mixing of these shallow waters with partially evaporated soil water enriched in ^{18}O, or that such evaporated waters were volumetrically insignificant. Another example: the slight ^{18}O-depletion of surface runoff relative to 30 cm interflow at 12 and 20 h may reflect the greater amounts of early isotopically enriched rain water lost to filling surficial soil storages than lost to filling soil pores at 30 cm. Table II shows that pore spaces in soils at 0–1 cm were filled several hours earlier than the soils at 1–2 cm, which is also consistent with the lower $\delta^{18}O$ values of surface runoff relative to shallow interflow. An alternate explanation, that the lower values are due to the addition of pre-event waters with $\delta^{18}O$ values lower than $-6 \pm 1‰$, is unlikely because the shallow waters would be expected to be more evaporatively enriched in ^{18}O than $-6‰$ and because the amounts of pre-storm water in these soils are volumetrically insignificant.

The question of preferential storage of different time-fractions of rain is very important because of the LARGE amounts of rain going into storage: 45% of the total rain by 32 h has gone into storage. The amount going into storage varies during the storm, with 100% of the rain from 4 to 6·5 h—a total of about 20 mm of rain—going into storage before flow starts (Figure 3). This first 20 mm of rain has a volume-weighted $\delta^{18}O$ value of $-10{\cdot}6‰$; if it goes into storage and is not displaced to form discharge by later rain, the $\delta^{18}O$ values of the 'residual' or mobile cumulative rain at 12 h, 20 h, and 32 h are $-12{\cdot}1‰$, $-12{\cdot}4‰$, and $-11{\cdot}5‰$ respectively. These values are 0·2 to 0·5‰ lower than the comparable total cumulative rain $\delta^{18}O$ values in Table IX. Hence, the consequence of storage of initial rain water enriched in ^{18}O is that the calculated amounts of new water in Table IX decrease by about 7% at 12 h, 7% at 20 h, and 3% at 32 h. Only one of these event values (Table IX) is greater than 100% (103% for surface runoff at 12 h), an improvement over the original values where five values for percent event-water (calculated using $\delta^{18}O$) were over 100% (Table VII). Hence, assuming that the first 20 mm of rain goes into storage improves these hydrograph separations and is probably a valid assumption.

Table IX. Calculated cumulative amounts of event water[a]

Trough	Event water (%)		
	12 h	20 h	32 h
Surface runoff	103	99	95
30 cm	98	96	98
60 cm	88	78	75
100 cm	72	58	51
Total flow	95	88	85

[a] Values calculated using $\delta^{18}O$ values and assuming the initial 20 mm of rain went into storage.

Although $10 \pm 5\%$ of the total flow for the three calculation times is pre-event water (Table VII), the displacement of pre-event water by storage of about 55% of the new rain in the catchment has had a negligible effect on the amount of pre-event water remaining in the system (~97%). This is because the amount of pre-event water stored in the soil (290 mm) was four to five times greater than the total amount of water discharged from the catchment. The $\delta^{18}O$ of the soil water at the end of the storm is only about 1‰ lower than the original pre-event water.

A perceptual model of internal hillslope processes

The isotope separations indicate that $90 \pm 10\%$ of the total flow is event rain water and the hydrologic response (Table VII) show that about 80% of the flow is quickflow. Hence, almost all the quickflow must be rain, but not all the rain is quickflow. The dominant flow mechanism in this small catchment changes over the event and spatially. Immediately after the onset of intense rain, rain water reached the troughs via both surface runoff and bypass flow through soil cracks in the 0–30 cm layer. Although the contact time with the soil was short (flow-peak lag times of tens of minutes), the rain flowing along the surface and shallow flowpaths picked up concentrations of solutes approaching the concentrations seen in deeper soil waters. At several localities, deeper macropores allowed rain to penetrate rapidly to the bedrock surface where groundwater mounds—largely composed of rain water—progressively developed (Figure 7) and backed-up into the matrix (as per McDonnell, 1990, 1997; Kendall and Gu, 1992; Peters *et al.*, 1995; Tani, 1997). Chemically (but not isotopically), these waters were pre-event with higher concentrations of solutes than interflow or saturated flow samples (Figure 9). In other localities, infiltration of event rain that fell at the surface and resulted in the downward displacement of soil water and the development of groundwater mounds with pre-storm chemical and isotopic compositions. As the water table rises, the percentages of pre-event water in both groundwater and saturated flow samples gradually increased; during draining of the catchment, slower matrix flow appears to be the dominant flow mechanism.

Other workers have observed post-peak transitions from macropore (bypass) flow to predominantly piston (matrix) flow (Van Stiphout *et al.*, 1987; McDonnell, 1990; Buttle and Sami, 1990) The uneven development of the saturated zone (i.e. mounding) and variability in groundwater and saturated flow compositions supports the view that water is not necessarily infiltrating in a well-defined manner but instead may take complex routes, including upward transport and several transits through the various soil horizons (Christopherson and Neal, 1990; McGlynn *et al.*, 1999).

The ratio of event to pre-event water at Hydrohill is much higher than in most catchments discussed in Buttle's (1994) comprehensive review. Like the other new-water-dominated storms that have been studied in other catchments (e.g. Bonell *et al.*, 1990), this storm had a higher rain intensity than 'normal'. Indeed, infiltration excess overland flow occurred briefly during heavy rainfall bursts. Although this process does not generally occur in forested catchments, recent work has suggested that, during high intensity rainfall, such overland flow may occur immediately below the organic layer on the mineral soil surface (McDonnell *et al.*, 1991; Brown *et al.*, 1999).

The rapid hydrologic response of water from collectors at all depths is unusual, suggesting that flow *via* high conductivity zones and/or preferential flow must be important processes at all levels. About 20% of the rain (13·6 mm) discharges from the catchment from the 30 cm trough during the first 12 h of 5 July. This rather high value invokes questions about possible leakage along the walls of the troughs. Although a 20 cm lip between the troughs was installed and soils along the sides of the troughs were especially packed to prevent such leakage, settling of soil under the lip could have caused local ponding. The similarity in the hydrologic responses and isotopic compositions of 30 cm flow and surface runoff (Table VII) suggests that much of the water collected in the 30 cm trough may actually be derived from shallow soils that become saturated easily (Table II). An alternative explanation, that rain water penetrated cracks extending to 30 cm and then flowed laterally along some root-zone layer, is unlikely to have yielded the isotopic compositions and the rapid response observed. The similarity of the $\delta^{18}O$ compositions of both troughs (Figure 6b) to rain indicates that almost all the water is event rain; however, since chemical tracers suggest almost twice as much pre-event water at 30 cm as at the surface, the 30 cm flow has had considerably more contact with the soil. Thus, geochemical evolution along the flowpath is occurring without any corresponding isotopic shift. This is a key finding of this paper—that hydrograph separation is different between IHS and CHS, in contrast to the recent findings of Rice and Hornberger (1998).

For interflow to drain into a subsurface trough, a local saturated wedge (as first observed by Weyman (1973) and later by several other studies) must form and extend upslope from the trench face. Although vertical flow through macropores can rapidly deliver large amounts of water, the slow rate of lateral flow through the silt–loam soils is probably a rate-limiting factor, as governed by its low saturated hydraulic conductivity. The low flow at 60 cm, about 7% of the flow at 30 cm and 15% of the flow at 100 cm (Figure 4), suggests that interflow is not a major flow component below the soil surface 'saturated layer' that apparently discharges into the 30 cm trough. Because of the lack of layering in this deeper interval, the 60 cm trough can be considered to be in the 'shadow' of the 30 cm trough. Although any fractures that allow water to penetrate to 100 cm obviously give rain water access to the soils at 60 cm as well, the soil–bedrock interface provides an ideal flowpath for lateral flow, promoting more flow into the 100 cm trough than would occur by interflow alone.

There appears to be two broad 'types' of chemically different (but not truly distinctive) pre-storm water, a less-saline water that is characteristic of rapidly responding flowpaths that deliver water to the troughs, and a more-saline water that is characteristic of slower matrix flow. Explanations for this dichotomy include: differences in the relative amounts of constant-composition pore waters mobilized by the different mechanisms transporting event water, differences in the relative amounts of variable-composition pore waters of variable mobility incorporated by the different flow mechanisms, or differences in the amounts of new solute material that can be dissolved from soil surfaces (i.e. surface to pore-volume ratio) by waters travelling along different flowpaths. We do not have the data necessary to test these hypotheses. The more-dilute waters may reflect locations where persistent macropores allow event rain water to pond at the bedrock and rapidly create positive pore pressure and a back-up of saturation (transient groundwater mounds) into the soil column. The groundwater thus formed in these areas would incorporate little long-residence time water and would contribute sizable amounts of rapid runoff to the troughs. On the other hand, less-dilute waters would form in areas devoid of macropores where progressive displacement of old longer-residence time waters by infiltrating rain water slowly causes saturated zones to develop at the aquiclude. These more-saline waters would mainly respond as slow-flow. Bishop (1991) also found that waters rapidly transported along 'spate-specific flowpaths' at Svartberget acquired a chemical signature distinct from water moving more slowly by matrix flow.

In this conceptual model, pore waters in the unsaturated-zone and transient groundwater almost always will have higher concentrations of solutes than the interflow and saturated flow that drain into the troughs and are fed primarily by zones with the shortest residence times and highest transmissivity. Burns *et al*. (1998) reported similar findings for a trenched hillslope at the Panola catchment. Between storms, immobile or less-mobile waters exchange isotopically with the event mobile pore waters, and react chemically with the grain surfaces and thereby increase solute loads. By analogy, this model may explain why baseflow in natural catchments is also relatively uniform in composition and typically more dilute than groundwater—because baseflow is derived from the most mobile 'old' pre-event water in the system.

Although this scenario appears valid when comparing the isotopic and chemical compositions of groundwater with the saturated flow samples in the troughs, it fails to explain the chemical compositions of pre-event water in groundwater. The pre-event water in groundwater with more isotopically old water might be expected to be more saline than pre-event water in groundwater, where there is little old water; however, the calculated chemical compositions of pre-event water in groundwater show the opposite pattern (Figure 9b). Wells seeing high but decreasing proportions of rain water derive their pre-event waters and/or salt loads from different reservoirs or flowpaths than wells that see very little event water. These calculations reinforce the point that there can be very large ranges in the chemical compositions of old pre-event pore waters in different zones or flowpaths within the catchment.

CONCLUSIONS

The Hydrohill experimental catchment provides a unique opportunity to investigate processes taking place within a catchment. Because of all the instrumentation, detailed information about spatial and temporal changes in amounts and chemical and isotopic composition of soil water, groundwater, and subsurface flow from several horizons is available. This permits comparison of several types of hydrograph separation model, with independent knowledge of the amounts and compositions of water present in different storages and flowing along different pathways, and calculation of water budgets.

The water budgets can account for $98 \pm 7\%$ of the event rain water in the catchment in terms of discharges and changes in storages, and can account for $99 \pm 2\%$ of the total 'input' water. Achieving approximate closure on water budgets allows the unprecedented calculation of catchment isotope mass balances. Despite the large amount of rain that fell (120 mm) over a 24 h period, infiltration and subsequent storage of 55% of the event water displaced only about 3–5% of the pre-event water out of the catchment. Only 10% of the total flow is pre-event water, mostly derived from saturated flow from deeper soils. The average $\delta^{18}O$ of groundwater at the end of the storm is about 1‰ lower than the pre-event water; however, it appears that the event and mixed pore-waters are very heterogeneously distributed. Thus, the remaining water in the unsaturated zone available to mix with the next storm water shows considerable (~4‰ in groundwater) spatial and vertical variation in isotopic composition. If this much variability existed in the unsaturated zone prior to the 5 July storm, then the use of -6 ± 1‰ for the soil-water component may have resulted in erroneous calculated amounts of event water in the subsurface samples. In addition, depending on the rate of isotopic exchange in pore waters, this heterogeneity could cause substantial difficulties for hydrograph separations of subsequent storms. Another problem is that there is evidence that rain water with a relatively high $\delta^{18}O$ value from the beginning of the storm is preferentially stored in shallow soils. This is a minor violation of one of the critical assumptions of isotope hydrograph separations and results in 7% change in the estimated amount of new water in runoff prior to 21 h.

Downslope transport of infiltration water *via* macropores, displacement of pre-event unsaturated-zone water by matrix flow, and mixing of these two waters has caused widespread temporal and spatial variability in the isotopic and chemical compositions of interflow, saturated flow, groundwater, and post-storm unsaturated-zone water in this artificial catchment. The variability of rain and unsaturated-zone samples can pose substantial difficulties for the use of stable isotopes for tracing sources and flowpaths of water contributing to stormflow. If hillslope waters contribute much water to streams, then the conventional isotope hydrograph separation technique will need to be modified to include source components with isotopic and chemical compositions that may be temporally and spatially variable, and transit times neither constant nor instantaneous, and whose flowpaths may shift from predominantly bypass flow to matrix flow during the storm depending on rain intensity and amount of water stored in the soil zone.

Despite considerable spatial heterogeneity in the subsurface wetting-up of the experimental grassland catchment, uneven development of the saturated zone, variability in the sources of water (as indicated fairly unambiguously by the $\delta^{18}O$ values), and transitions between macropore and matrix flow, the discharge response is quite linear for all four troughs. Saturated flow is composed mostly of slow-flowing pre-event water, but includes some event water that has mixed with the older stored water. The magnitude of the storm studied is certainly a contributing factor to the event-water dominance, due to infiltration excess overland flow during high-intensity rain bursts.

Although the relative amounts of surface runoff and subsurface flow contributing to total discharge from the catchment calculated using chemical tracers closely match the actual measured amounts of surface runoff and subsurface flow, the agreement appears to be coincidental. Even surface runoff and macropore flow from shallow soil responding as quickflow and composed almost entirely of rain water are able to pick up loads of solutes similar to concentrations seen in subsurface flow. Therefore, chemical tracers (such as Cl and SiO_2) are poor indicators of both water source and specific flowpaths in this catchment, yielding only qualitative information about contact time with the soil.

There appear to be two broad types of chemically old water in the catchment: (1) a water developed by displacement of pre-event water by event water travelling slowly downwards through the soil as matrix flow; and (2) a water derived from rapid transport of largely rain water to the bedrock via macropores, causing a back-up of transient groundwater that moves upwards into the soil profile and incorporates short-residence-time pore waters. The first type looks isotopically and chemically pre-event and would be classified as slowflow, whereas the second group contains more event water and lower concentrations of salts, and contains both quick-flowing and slow-flowing components. Waters from this second type appear to be the main source of saturated flow to the troughs. Because these waters are the result of differences in local conductivity, the site-specific chemical and isotopic characteristics thus produced may persist over long time periods. The isotopic signatures of individual rain storms may be preserved in some places and rapidly blurred in others. It is clear that more information about isotopic exchange rates in pore waters is required to assess the impact of this variability on hydrograph separations.

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