Hydrograph separation using continuous open system isotope mixing

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Abstract. We propose a new hydrograph separation method for runoff source modeling based on continuous open system isotope mixing using a variable source area and three isotopic reservoirs. The three reservoirs are (1) direct precipitation on saturated areas, (2) a near-stream saturated zone, and (3) subsurface water in upslope areas. The reservoir sizes and isotopic compositions evolve due to continuous, open system mixing. Streamflow is composed of rainfall on saturated areas and water exfiltrated from the near-stream saturated zone. The contributing source fractions are determined using the observed isotopic compositions of the stream and the modeled isotopic compositions of the contributing reservoirs, which are functions of time. The near-stream saturated zone receives inflow from upslope areas which are not surface saturated. The surface-saturated area changes dynamically based on the difference between lateral inflow and contributions to streamflow from the near-stream saturated zone. The upslope zone (reservoir 3) evolves by mixing with rainfall. This hydrograph separation method requires (1) a function which relates the amount of water stored in the near-stream saturated zone to saturated area, (2) a function which relates saturated area fraction to total streamflow, and (3) knowledge of the water storage capacity in reservoirs 2 and 3. The hydrograph separation method was applied to oxygen isotope data for rainfall and runoff during a 36-hour storm at the Gårdsjön F1 catchment in southwestern Sweden. The hydrograph separation method was used to estimate time-dependent streamflow contributions due to overland flow of storm rainfall and subsurface flow of mainly preevent water. We also used the separation method to estimate parameters for relations between saturated area fraction and streamflow, and saturated area and subsurface water storage. We show that streamflow contributions from overland flow may be described by a simple analytic function of antecedent conditions and catchment parameters.

Introduction

Water may be routed within catchments via different types of flow paths and physical mechanisms. Some suggested mechanisms for rapidly delivering water to streams include saturation overland flow [*Dunne and Black*, 1970], macropore flow [*Mosley*, 1979], displacement flow via groundwater ridging [*Sklash et al.*, 1986] with hydraulic gradients enhanced by a capillary fringe response [*Gillham*, 1984], and rapidly increasing transmissivity due to a large increase in the hydraulic conductivity near the ground surface [e.g., *Rodhe*, 1987]. Stable isotope tracing of streamflow sources, in conjunction with field hydrometric measurements, provides the capability to test hypotheses about contrasting mechanisms of runoff generation, flow path utilization, and catchment water storage capacities. Stable isotopes have been used as tracers to infer the relative contributions to

runoff from soil water, groundwater, storm precipitation, and snowmelt [e.g., *Rodhe*, 1987; *DeWalle et al.*, 1988; *McDonnell et al.*, 1990; *Wels et al.*, 1991]. Knowledge of flow path utilization and their fluxes is important for improving physical and chemical models of runoff generation, stream water composition, and solute transport in catchments.

The use of stable isotopes (notably oxygen 18 and deuterium) for hydrograph separation relies on the assumed conservative behavior of stable isotopes in water during flow through a catchment: The isotopic composition changes only by mixing. Hydrograph separations based on chemical tracers, on the other hand, may or may not rely on conservation of the tracer. If the tracer reacts with the surrounding material, changes in the concentration of tracer in water may give information about the flow paths [e.g., *Wels et al.*, 1991]. This paper considers only hydrograph separation based on conservative nonreactive tracers.

The most direct method of hydrograph separation may be used to apportion stream runoff to two (or more) isotopically

distinct sources: (1) water produced during a rain or snow-melt event (also called "new" water) and (2) soil water or groundwater already in the catchment at the start of the event (also called "old" or "preevent" water). The fraction of "old" water is a minimum value for the fraction of subsurface water in runoff, because some of the "new" water may use subsurface flow paths en route to the stream. In a more physical approach, stream water could be separated into flow path–related sources (e.g., soil water, groundwater, and rainwater that has reached the stream as overland flow).

In the two types of hydrograph separation described above, the isotope ratios of the water reaching the stream from each of the sources must be known at all times from measurements or calculations. The isotopic composition of coeval rainfall or snowmelt can be used as an approximate value for the surface water component only if (1) the temporal variation of rain or meltwater isotopic composition is small, (2) the residence time of rain or meltwater on the ground surface is short, and (3) return flow (subsurface to surface) is negligible or its effects can be estimated by other means. However, the temporal variations of isotope ratios of subsurface water reaching the stream cannot be measured. Instead, the isotopic compositions of subsurface water sources are assumed to be constant and equal to those of soil water, groundwater, or stream water before the event, or the compositions are assumed to vary according to simple assumptions [Hooper and Shoemaker, 1986] or a simple mixing model [e.g., Rodhe, 1987]. The resulting hydrograph separations depend on the validity of the required approximations, as well as the precision, accuracy, and frequency of sample measurements relative to the temporal and spatial scales of variation. Large variations in isotopic composition are common during rainstorms [McDonnell et al., 1990] and snowmelt [Herrmann et al., 1981]. Thus, apart from problems related to spatial variations, measurement errors, and source discrimination, there are two important temporal problems for hydrograph separation using isotope tracers: (1) how to take into account observed temporal variations in the isotope ratios of water and (2) how to correctly describe temporal changes of the subsurface components caused by infiltration of rainfall [e.g., McDonnell et al., 1991] or snowmelt. Isotope mixing equations developed for "batch" mixing are not generally applicable or appropriate to hydrograph separation problems in which continuous mixing and changes in storage are important. We propose that continuous open reservoir isotope mixing represents a more realistic approach which is suitable for hydrograph separation.

The purpose of this paper is to describe a new hydrograph separation method which takes into account temporal variations in the isotopic compositions of rainfall or snowmelt and of the reservoirs which contribute to streamflow. The approach is fundamentally different from previous methods based on two- and three-reservoir batch-mixing models because in this paper the isotopic reservoirs vary continuously in composition and size and because the amounts of water and tracer are conserved at all times. We describe how to obtain a continuous storm hydrograph separation for a moderately complex case. We show that the hydrograph flux separation with this approach is sensitive to the saturated area, to catchment water storage capacity, and to initial conditions.

This paper uses the general terminology of Chorley [1978]

and Hewlett [1982], as set forth by Kennedy et al. [1986]. It is necessary to review several terms that are important for understanding the present paper because of inconsistent use of these terms in the literature.

By soil water we mean water in the soil or bedrock with a pressure smaller than that of the atmosphere. By groundwater, we refer to water in the soil or bedrock with a pressure above or equal to that of the atmosphere. By saturated area we mean the area of the catchment in which the groundwater zone reaches the ground surface. This term refers to a surface area, not a volume. The term surface-saturated zone refers to the saturated volume beneath the saturated area. It is physically located adjacent to stream sections or along a hollow axis that is surface saturated. Here, the word "zone" is used to imply a volume and "surface-saturated" is used as a modifier to describe the defining attribute. The term subsurface water refers to all water (regardless of its degree of mobility) below the ground surface, including both soil water and groundwater. By old water we mean water existing in the catchment (subsurface and surface water) before the onset of rain or snowmelt. By new water we mean water (rain or snowmelt) entering the catchment during the event under study.

Hydrograph Separation Based on Variable Source Areas

The hydrograph separation method in this paper is based on the variable source area hypothesis of streamflow generation [Hewlett and Hibbert, 1967]. Figure 1 illustrates, using a hillslope cross section, our method of defining catchment reservoirs for purposes of hydrograph separation in the context of the variable source area hypothesis. The mathematical description is in the section on mass balance equations. There are three water reservoirs: (1) direct precipitation on saturated areas (including the stream channel), (2) subsurface water in the near-stream surface-saturated zone, and (3) subsurface water (unsaturated and saturated zones) in areas upslope of the near-stream surface-saturated zone. The hydrograph separation method assumes continuous, open system mixing and evolution of the three reservoirs as required by conservation of water and isotopic tracer. Streamflow is assumed to be generated by direct precipitation on saturated areas and water exfiltrated from the near-stream saturated zone. The proportions of instantaneous runoff from these sources are determined by the isotopic composition of stream water relative to the instantaneous isotopic compositions of the contributing reservoirs. The near-stream saturated zone (reservoir 2) is replenished from upslope areas which are not surface saturated (reservoir 3). New precipitation is routed to and mixes isotopically with water in reservoir 1 (direct precipitation on saturated areas) and reservoir 3 (upslope areas) in amounts which vary in proportion to the saturated area fraction. The saturated area changes dynamically based on the difference between replenishment of reservoir 2 (near-stream surface-saturated zone) by inflow of subsurface water from reservoir 3 (upslope zone) and discharge to the stream. The calculated fluxes to the stream are based on the measured total streamflow and on the measured isotopic composition of the stream water relative to calculated compositions of the reservoirs. The reservoir isotopic compositions are based on mass
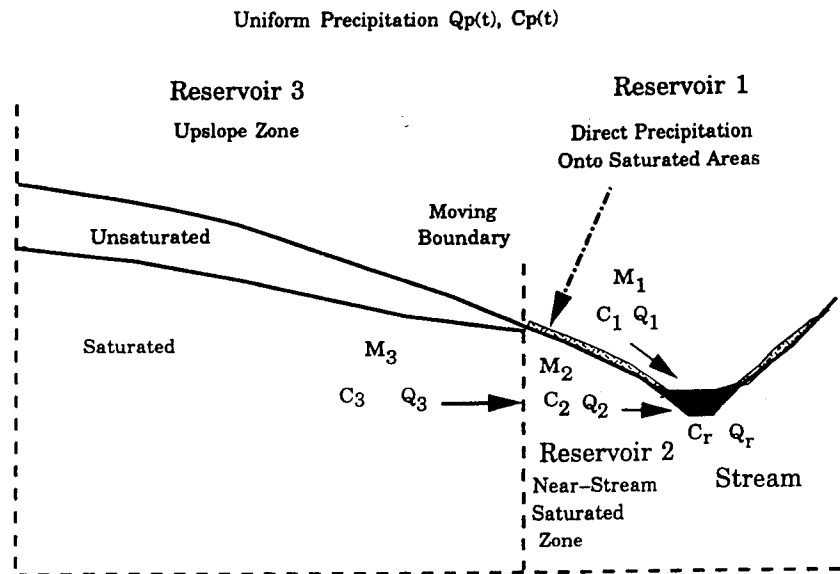
Figure 1. Schematic diagram of continuous open system isotope mixing model. Arrows indicate model flux directions. Dashed line indicates boundary limiting surface-saturated areas of catchment. Hachured area is surface saturated. Solid area represents stream.

balance equations for open system isotopic mixing developed for a variable source area.

Although we make few assumptions regarding how water is transmitted between reservoirs and how it is transmitted from reservoirs to stream channels, we assume the following:

1. The precipitation flux and its isotopic composition may vary with time, but do not vary spatially over the catchment.

2. All precipitation on surface-saturated areas is added to reservoir 1 and mixes isotopically with earlier rainfall remaining on these areas. The water in reservoir 1 remains on the catchment for variable, but unspecified, periods of time.

3. All precipitation on non-surface-saturated areas of the catchment infiltrates and mixes isotopically with water in reservoir 3.

4. The mass of water held in reservoir 2 is defined by the saturated zone water storage capacity, which is a function of the saturated area.

5. Complete mixing within the reservoirs is assumed (i.e., the effect of spatial variations of isotopic composition within the reservoirs is assumed to be unimportant at the scale responsible for catchment runoff).

6. The effects of evapotranspiration, including interception, on mass fluxes and isotopic composition are not considered. The effect of interception may, however, be accounted for if the observed precipitation is simply replaced by observed throughfall.

7. There is no mass transfer, isotopic mixing, or isotopic exchange between reservoirs 1 (direct precipitation on saturated areas) and 2 (near-stream surface-saturated zone). On many catchments, surface discharge of groundwater is common in surface-saturated areas. This simplification could lead to errors in hydrograph separations if there is any mixing between these two reservoirs.

Mass Balance Equations

The equations below describe the evolution of the water reservoirs and their isotopic compositions in response to modifications by precipitation and streamflow. We describe in the next section how the mass balance equations may be solved to infer the relative contributions to streamflow from the catchment water sources. In this paper, all reservoir sizes and water flows are normalized to the catchment area. The notation section includes a list of variables and their units of measure.

Components of Stream Runoff

The catchment runoff, Q_r, is equal to the sum of fluxes from the assumed streamflow sources:

$$Q_r(t) = Q_1(t) + Q_2(t) \qquad (1)$$

Q_1 and Q_2 are the runoff contributions from reservoir 1 (direct precipitation on saturated areas) and reservoir 2 (surface-saturated zone), respectively. If the mass fraction of runoff from reservoir 1 is $f_1(t)$, we can write the source fluxes in terms of $Q_r(t)$:

$$Q_1(t) = f_1(t)Q_r(t) \qquad (2a)$$

$$Q_2(t) = (1 - f_1(t))Q_r(t) \qquad (2b)$$

It is the purpose of this paper to show how $f_1(t)$ may be inferred from a time series of isotopic and hydrometric measurements of rainfall and runoff.

The isotopic composition of runoff, C_r, is equal to the ratio of the sum of flux-weighted tracer concentrations in the sources contributing to the total flux:

$$C_r(t) = \frac{Q_1(t)C_1(t) + Q_2(t)C_2(t)}{Q_r(t)} = f_1(t)C_1(t)$$

$$+ (1 - f_1(t))C_2(t) \quad (3)$$

In (3), C_1 and C_2 are the isotopic compositions of reservoirs 1 and 2, respectively. We assume no direct contribution of streamflow from reservoir 3 (upslope zone). However, the upslope zone influences the isotopic composition of runoff owing to the flux of water from isotopic reservoir 3 to reservoir 2 (see equations (10) and (11)). Note that $f_1(t)$ may be inferred from isotopic measurements, but only if $C_1(t)$ and $C_2(t)$ are known. We calculate $C_1(t)$ and $C_2(t)$ using knowledge about the amount and isotopic composition of water in the catchment at the start of the storm and conservation of mass.

Direct Precipitation on Saturated Areas (Reservoir 1)

Water mass. The mass $M_1(t)$ of direct precipitation on saturated areas (normalized to the entire catchment area) at time t is governed by

$$\frac{1}{\rho} \frac{dM_1}{dt} = a_s Q_p - Q_1 \quad (4)$$

where Q_p is the precipitation rate, Q_1 is the runoff from reservoir 1, a_s is the surface-saturated area fraction, and ρ is the density of water. In (4), runoff of direct precipitation on saturated areas is generally not equal to the contemporary precipitation rate. Equation (4) incorporates (via the storage term, $M_1(t)$) the facts that catchments have finite surface-saturated areas and that storm runoff from such areas lags precipitation. Equation (4) is subject to the initial condition $M_1(0) = 0$ or some other value, which states that the mass of surface water on the catchment is known at the start of the runoff event. An additional constraint is that $M_1(t)$ must be nonnegative for all t.

Tracer conservation. The amount $T_1(t)$ of tracer in reservoir 1 at time t (normalized to the entire catchment area) is governed by

$$\frac{1}{\rho} \frac{dT_1}{dt} = a_s Q_p C_p - Q_1 C_1 \quad (5)$$

Equation (5) is subject to the initial condition $T_1(0) = M_1(0)C_1(0)$, which states that the amount of tracer in reservoir 1 is known at the start of the runoff event. Equation (5) describes the result of isotopic mixing of new precipitation with earlier precipitation of variable isotopic composition retained on the surface of the catchment, after subtracting the flux of tracer to the stream.

Isotopic composition. The isotopic composition $C_1(t)$ of water in reservoir 1 (derived from direct precipitation on saturated areas of the catchment) at time t is

$$C_1(t) = \frac{T_1(t)}{M_1(t)} \qquad M_1(t) > 0 \quad (6)$$

Whenever $M_1(t) = 0$, $C_1(t)$ is equal to $C_p(t)$ if $Q_p(t) > 0$ and undefined otherwise. In (6) the isotopic composition of surface water varies with time and is generally different from that of current precipitation, the average of earlier precipitation, and the average of whole event precipitation.

Surface-Saturated Zone (Reservoir 2)

Water mass. The mass $M_2(t)$ of water in reservoir 2 (saturated zone) per unit catchment area at time t is governed by

$$\frac{1}{\rho} \frac{dM_2}{dt} = Q_3 - Q_2 \quad (7)$$

where Q_3 is the water flux from reservoir 3 to reservoir 2. Equation (7) is subject to specification of initial values of $M_2(0)$. When $Q_3 > Q_2$, the saturated area must increase, and the converse is also true. Accordingly, the mass balance for reservoir 2 may be written in terms of the derivative of the saturated area fraction:

$$\frac{dM_2}{dt} = \frac{dM_2}{da_s} \frac{da_s}{dt} \quad (8)$$

We define dM_2/da_s, which is the derivative of the saturated zone water storage capacity M_2 with respect to saturated area fraction, to be the marginal water storage capacity. The use of this function links the soil water storage capacity at saturation (soil thickness times porosity) to saturated area. Use of (8) requires specification of a function (see (17)) to represent $M_2(a_s)$. For further discussion, see the subsection on water storage capacity. Substituting (8) into (7), we obtain

$$\rho(Q_3 - Q_2) = \frac{dM_2}{da_s} \frac{da_s}{dt} \quad (9)$$

which illustrates the relation between the water balance in the near-stream saturated zone (left side of equation) and the product of the marginal water storage capacity in the surface-saturated zone and the rate of change of surface-saturated area fraction (right side of equation). Whenever the right side of (9) is zero (e.g., saturated area constant) and Q_2 is positive, there must be a positive flux Q_3 (equal to Q_2) from the upslope zone (reservoir 3) to the near-stream surface-saturated zone (reservoir 2) simply to maintain the saturated area at a constant value.

The net flux $Q_3(t)$ from reservoir 3 to reservoir 2 may be obtained by rearranging (9):

$$Q_3 = Q_2 + \frac{1}{\rho} \frac{dM_2}{da_s} \frac{da_s}{dt} \quad (10)$$

The excess (or deficit) of Q_3 relative to Q_2 is a mass transfer between reservoirs 2 and 3 which represents increase (or decrease) in the surface-saturated area. Evaluation of (10) requires knowledge of $a_s(t)$.

The functional form of the saturated area fraction, $a_s(t)$, is not an integral part of the hydrograph separation method, but an empirical function is required to apply this method to specific catchments. For example, one may assume a simple (and possibly incorrect) linear relation between the catchment saturated area fraction a_s and streamflow Q_r (see the subsection on catchment saturated area fraction and (19)).

Tracer conservation. The amount of tracer in reservoir 2 (near-stream saturated zone), $T_2(t)$, normalized to the entire catchment area, is governed by

$$\frac{1}{\rho} \frac{dT_2}{dt} = Q_3 C_3 - Q_2 C_2 \quad (11)$$

Equation (11) is subject to the initial condition $T_2(0) = M_2(0)C_2(0)$. Equation (11) describes how the isotopic reservoir changes as a result of differences between inflow and outflow, weighted by their respective compositions. Bidirectional mass transfer and isotopic mixing between reservoirs 2 and 3 is supported in this separation method through the mass balance expressed in (11) and the form of Q_3 given in (10).

Isotopic composition. The isotopic composition of reservoir 2 (surface-saturated zone) is

$$C_2(t) = \frac{T_2(t)}{M_2(t)} \qquad M_2(t) > 0 \qquad (12)$$

where the numerator and denominator may be evaluated from (11) and (7), respectively.

Upslope Zone (Reservoir 3)

Water mass. The mass of water in the non-surface-saturated zone, $M_3(t)$, normalized to the catchment is governed by

$$\frac{1}{\rho}\frac{dM_3}{dt} = (1 - a_s)Q_p - Q_3 \qquad (13)$$

The terms on the right represent precipitation on non-surface-saturated areas and the net flux (Q_3) from reservoir 3 to reservoir 2 (see (10)).

Tracer conservation. The amount of tracer in reservoir 3, $T_3(t)$, normalized to the catchment area, is

$$\frac{1}{\rho}\frac{dT_3}{dt} = (1 - a_s)Q_pC_p - Q_3C_3 \qquad (14)$$

Equation (14) is subject to the initial condition $T_3(0) = M_3(0)C_3(0)$. Equation (14) describes how this isotopic reservoir evolves by mixing tracer in current precipitation with tracer already in the reservoir. The term Q_3 represents the net mass transfer to reservoir 2. As noted above, the second term accommodates bidirectional mass transfers through the representation of Q_3 in (10).

Isotopic composition. The isotopic composition of water in reservoir 3 at time t is

$$C_3(t) = \frac{T_3(t)}{M_3(t)} \qquad M_3(t) > 0 \qquad (15)$$

where the numerator and denominator may be evaluated from (14) and (13), respectively.

Saturated Area, Storage Capacity, and Discharge Relations

The surface-saturated area varies with time during rainstorms and snowmelt in natural catchments. Accordingly, the amount of water stored in the near-stream surface-saturated zone also varies. The amount of water stored in the near-stream saturated zone may not be strictly proportional to the surface-saturated area. We offer several equations for the purposes of representing (1) the distribution of water storage capacity in the catchment, including the near-stream surface-saturated zone (equation (17)); (2) the marginal water storage capacity (equation (18)); (3) the surface-saturated

area fraction (equation (19)); and (4) the rate of change of surface-saturated area fraction (equation (20)).

Water Storage Capacity

In (8)–(10) we included a term, dM_2/da_s, to describe how water storage in the near-stream surface-saturated zone varies with the surface-saturated area fraction (a_s). A general form of a relation between M_2 and a_s is the following:

$$M_2(a_s) = \rho \int_0^{a_s} \phi(a_s)D(a_s) \, da_s \qquad (16)$$

where D is the thickness of the soil, ϕ is profile mean value of soil porosity (all water in the ground is assumed to take part in the flow and mixing), and ρ is the density of water. For illustration purposes in this paper, we assume a power law relation between M_2 and a_s given by

$$M_2(a_s) = \rho\phi Da_s^n \qquad (17)$$

where D is a representative soil thickness, ϕ is a representative soil porosity, and n is a parameter. The product of the first three coefficients has units of mass of H_2O per unit area. The product ϕD, which has units of water depth, is equal to the mean water storage capacity (at saturation) in the catchment. In (17) the special case $n = 1$ describes a catchment which has a uniform water storage capacity. With $0 < n < 1$, the first derivative of M_2 with respect to a_s is positive and the second derivative is negative. This is an important property, as it represents a catchment which has greater saturated zone water storage capacity per unit area at small values of a_s than at larger values of a_s. This case is satisfied in catchments for which the product of soil thickness and porosity decreases with increasing saturated area. Such a relationship seems reasonable, particularly in steep catchments with thinner soils at higher elevations. However, the validity of (17) has not been established for any catchment.

Assuming (17) is valid for some unknown value n, the marginal water storage capacity in the surface-saturated zone is given by

$$\frac{dM_2}{da_s} = n\rho\phi Da_s^{n-1} \qquad (18)$$

Equations (8)–(10) require use of either (18) or an equivalent empirical or theoretical relation that is appropriate for the catchment under study [e.g., *Dunne et al.*, 1975].

Catchment Saturated Area Fraction (a_s)

An empirical relation between the surface-saturated area fraction, a_s, and another time-dependent hydrologic variable (e.g., Q_r) is required to evaluate da_s/dt in (8)–(10). The saturated area fraction a_s may be represented as a function of stream discharge, Q_r [e.g., *DeWalle et al.*, 1988]. For purposes of illustration in this paper, we assume a simple linear relation between a_s and Q_r:

$$a_s = a_0 + kQ_r \qquad (19)$$

The constants a_0 and k in (19) must be estimated from empirical relations between catchment discharge and surface-saturated area. The saturated area fraction $a_s(t)$ may be calculated from (19) and $Q_r(t)$. Then, we may write

$$\frac{da_s}{dt} = k \frac{dQ_r(t)}{dt} \qquad (20)$$

Equations equivalent to (19) and (20) appropriate to specific catchments are required to apply the stream hydrograph separation method described in this paper.

Algorithm

Our objective is to infer the function $f_1(t)$ (the inferred fraction of total runoff due to direct precipitation on surface-saturated areas as a function of time t). Once $f_1(t)$ is known, the time-dependent runoff contributions from this source (Q_1, reservoir 1) and from the near-stream saturated zone (Q_2, reservoir 2) may be calculated from (2). Accordingly, the hydrograph separation technique requires determining the function $f_1(t)$ which satisfies the governing equations defined above for hydrologically significant parameter values.

Hydrograph separation by this technique requires five input quantities represented by functions constructed from a time series of measurements. These functions of time include the isotopic composition of runoff (C_r), the streamflow (Q_r), the precipitation rate (Q_p), the isotopic composition of precipitation (C_p), and the near-stream saturated area fraction (a_s). The saturated area fraction may be related to streamflow $Q_r(t)$ through a relation similar to (19).

There are 15 unknown variables and a set of 15 governing equations (equations (2a), (2b), (3), (4), (5), (6), (7), (10), (11), (12), (13), (14), (15), (18), and (19)). These variables and their governing equations (shown in parentheses following the variables) include the reservoir masses (M_1 (4), M_2 (7), M_3 (13)), tracer amounts (T_1 (5), T_2 (11), T_3 (14)), and isotopic compositions (C_1 (6), C_2 (12), C_3 (15)) of the reservoirs, water fluxes (Q_1 (2a), Q_2 (2b), Q_3 (10)), the fraction (f_1 (3)) of runoff from reservoir 1, the saturated area fraction a_s (19), and the marginal water storage capacity dM_2/da_s (18).

The required initial conditions are the masses of water (per unit catchment area) in the three reservoirs (M_1, M_2, M_3) and their isotopic compositions (C_1, C_2, C_3). Estimation of $M_2(0)$ requires knowledge of $a_s(0)$ and use of a relation between M_2 and a_s, such as (17). The catchment parameters required include the exponent n in (17) and the coefficients k and a_0 in (19). The initial isotopic compositions $C_2(0)$ and $C_3(0)$ may, for example, be assumed equal to the initial (preevent) isotopic composition of runoff, $C_r(0)$. Finally, we wish to emphasize that the accuracy of the hydrograph separation ultimately depends on the accuracy of estimated initial conditions and relations among water storage capacity, streamflow, and surface-saturated area in the catchment. However, the need to estimate initial conditions and reservoir sizes should not be more problematic than simply ignoring effects related to continuous, open system isotopic mixing in reservoirs of finite size.

The equations are solved at successive time steps to evaluate the variables f_1 (3), Q_1 (2a), Q_2 (2b), M_1 (4), T_1 (5), C_1 (6), a_s (19), dM_2/da_s (18), Q_3 (10), M_2 (7), T_2 (11), C_2 (12), M_3 (13), T_3 (14), and C_3 (15). The equations are solved by a finite difference scheme. The solution is reached at each time step whenever the model stream isotopic composition $C_r(t)$ calculated from (3) converges to the interpolated stream values at time steps based on a time series of measurements. The functions representing the compositions and fluxes preserve all of the variations included in the original observations.

The hydrograph separation program includes the capability to perform multiple hydrograph separations for user-defined ranges of catchment parameters (a_s, k, n, and ϕD) and initial conditions ($M_1(0)$, $M_3(0)$, $C_1(0)$). The quality of the separation is measured by the root mean square deviation of model stream isotopic compositions $C_r(t)$ from measured values. The program records the subset of catchment parameter values and initial conditions for which the assumed parameters can match the stream composition within a prescribed maximum error. If some of the catchment parameters or initial conditions are known accurately, some of the resulting hydrograph separations can be excluded from consideration. The inversion algorithm will also find the best fit among the suite of input values. However, the stream hydrograph separation problem does not have a unique solution in the absence of (1) narrow bounds on the catchment parameters and initial conditions or (2) additional hydrologic constraints. The hydrograph separation method described here can be used to estimate catchment parameters and their uncertainty. The values derived from modeling can be compared to values suggested by field observations. Any combinations of catchment parameters and initial conditions which (1) generate the observed temporal variations in stream isotopic composition, (2) produce model stream isotopic compositions which have root mean square (rms) errors less than the expected analytical precision, and (3) do not contradict other information about the catchment and relevant hydrologic processes are considered to be permissible values.

The inversion algorithm operates normally whenever the stream composition $C_r(t)$ is between $C_1(t)$ and $C_2(t)$. In such cases the equations are solved to obtain convergence (if possible) to within a prescribed maximum deviation (here, 0.002‰) from the stream composition. Such convergence, of course, exceeds the precision of the measurements by a factor of at least 10. There is one special situation which requires an exception to the inversion procedure. An exception ("composition out of range") occurs at any time step for which the stream runoff composition C_r is not between C_1 and C_2 (e.g., due to errors in the separation method, its parameters, or initial conditions or analytical errors or blunders). In this case, we assume a single contributing source and set $f_1(t)$ to 0 or 1, depending on which reservoir is closest in composition to that of the stream. This is an approximation which tends to minimize the difference between the model and measured stream compositions. However, the error of the old/new water separation increases as the difference in source reservoir compositions becomes small. If the errors are large, the reservoir compositions and sizes diverge from their correct values, resulting in a poor fit to subsequent stream compositions. In the example below, the exception-handling procedure was invoked for eight of 140 time steps. In all cases the isotopic composition of the stream differed from that of the near-stream saturated zone by 0.005–0.033‰ $\delta^{18}O$, and the resulting error must be very small.

Application

The hydrograph separation method was applied to data of *Rodhe* [1987] for the Gårdsjön F1 A rainfall event. This

Table 1. Gårdsjön Fl A Catchment Data and Storm Summary

Parameter	Value
Location	58°03′N, 12°02′E
Catchment area, ha	3.6
Elevation range, m above sea level	115–135
Mean precipitation, mm yr^{-1}	1140
Mean January temperature, °C	−2.8
Mean July temperature, °C	16.6
Storm duration, hours	36
Total storm rainfall, mm H_2O	56
Total storm runoff, mm H_2O	13.6
Peak 15-min rainfall rate, mm h^{-1}	6.0
$\delta^{18}O$ isotopic range, per mil SMOW	
Stream water	−9.5 to −10.5
Rainwater	−8.0 to −19.3

Data are from *Rodhe* [1987]. SMOW denotes standard mean ocean water.

Figure 3. Comparison of modeled and measured oxygen isotope composition of stream water for the Gårdsjön Fl A rain event. The measurements are from *Rodhe* [1987], and the simulated values are based on the hydrograph separation technique described in this paper.

catchment (Gårdsjön Fl), which is located in southwestern Sweden, has an area of 36 ha and is vegetated by coniferous forest [*Rodhe*, 1987]. The bedrock is mainly gneiss. Elevated and steep areas of the catchment are frequently free of soil, and in the lower parts and in the valley bottom the catchment is covered with at most a few meters of fairly coarse till soil. Table 1 lists details of the catchment and storm.

The Gårdsjön Fl A event was a frontal rainstorm of June 12–14, 1982, with a total rainfall of 56 mm falling at varying rates over a 36-hour period (Figure 2). The storm followed a long dry period. The isotopic composition of the rainfall (Figure 2) and that of the stream (Figure 3) varied in a complex way with time. Early rainfall was enriched in ^{18}O and late rainfall was depleted in ^{18}O relative to stream runoff (Figures 2 and 3).

There are three possible applications of the proposed hydrograph separation method. They are (1) to test the hydrograph separation method, (2) to estimate catchment parameters and initial conditions, and (3) to test the variable source area hypothesis for streamflow generation. Application 1 requires assuming that the catchment parameters and initial conditions are known precisely, that the variable source area hypothesis governs streamflow generation in the catchment, and that the true hydrograph separation is known
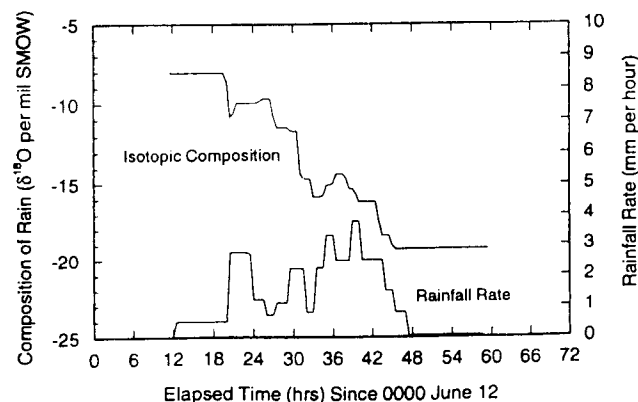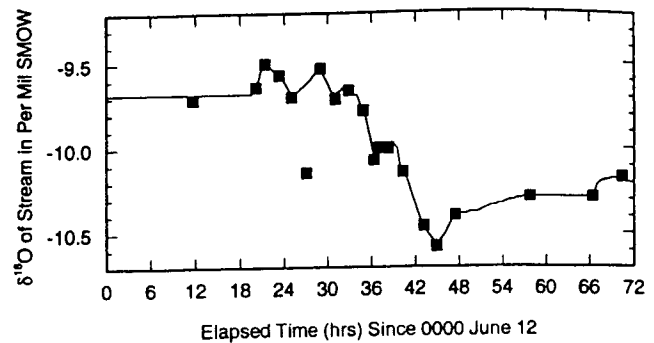
independently. Application 2 requires assuming that the hydrograph separation method is valid and that the variable source area hypothesis applies to the catchment. Application 3 requires assuming that the catchment parameters and initial conditions are known precisely and that the hydrograph separation method is valid. Our purpose is simply to illustrate case 2 and show how the hydrograph separation method might be used to infer bounds on catchment parameters and initial conditions.

Alternative hydrograph separations based on different combinations of catchment parameters and initial conditions were evaluated by determining the rms deviation of model values of stream isotopic compositions from measured values. We emphasize that agreement between modeled and measured stream compositions is always required for the separation algorithm to operate successfully. As the parameters and initial conditions deviate by greater amounts from their true (and unknown) values, the ability to perfectly match a time series of stream isotopic compositions decreases. The rms deviations provide a relative figure of merit for alternative hydrograph separations. Using the known precision of the stream isotopic measurements, rms deviations may be used to define the range of parameters and initial conditions which are compatible with the imprecise observations and assumptions detailed above.

Results and Discussion

First, we discuss why the hydrograph separation method proposed here might yield either no solution, one solution, or many solutions. Next, we discuss the estimated values of catchment parameters and initial conditions based on a purely mathematical solution. Finally, we describe how the shape of one solution to the mass balance equations might be explained in terms of the variable source area hypothesis, antecedent conditions, and time-dependent rainfall rates.

Nonuniqueness of Solution If Parameters Are Not Known Exactly

In simple two-component isotope hydrograph separation, there are two unknowns (the flows of old and new water in the stream) and two equations (binary mixing equations for total streamflow and tracer). Algebraically, there thus exists a unique solution whenever the stream composition is inter-

Figure 2. Rainfall rate in millimeters per hour during the Gårdsjön Fl A rainfall event and oxygen isotopic composition $\delta^{18}O$ in per mil SMOW [after *Rodhe*, 1987, Figure 8.9b].

mediate between the fixed old and new water isotopic compositions, although the underlying model may be a bad description of the real world.

In the more complex separation method presented here, there are 15 unknowns and 15 equations, and there may exist a unique mathematical solution. However, the initial conditions, the parameters in the catchment water storage function (17), and the relation between saturated area fraction and stream discharge (19) are not known exactly. Accordingly, except possibly when all of the initial conditions and catchment parameters are known exactly, the stream hydrograph separation problem does not have a unique mathematical solution. A family of solutions exists.

Purely mathematical solutions to the hydrograph separation equations result in very complex temporal variations of the mass fraction of surface water ($f_1(t)$) in the stream runoff. Whenever there is uncertainty about the correct catchment parameters or initial conditions, a large family of hydrograph separations must be considered. We varied the catchment parameters and initial conditions to identify solutions which match the stream isotopic composition with an rms error of less than 0.01‰ $\delta^{18}O$. Model values were interpolated to measurement times.

There is no guarantee that the parameters and initial conditions inferred from a mathematical solution which matches all observations is hydrologically realistic. Conversely, there is no requirement that realistic catchment parameters and initial conditions will lead to a mathematical solution which matches all observations. The data from Gårdsjön F1 A illustrate the latter case. We could not match the measured stream isotopic composition of −10.14‰ $\delta^{18}O$ at 27 hours elapsed time (Figure 3) using any reasonable combinations of catchment parameters and initial conditions. At the same time, the oxygen isotopic composition of the saturated zone reservoir (C_2) was probably about −9.68‰ standard mean ocean water (SMOW), and the composition of prior rainfall (assuming no losses) would have been about −9.59‰ SMOW. The isotopic composition of coeval rainfall was −10.78‰. If the measured stream composition of −10.14‰ is correct, it would require either (1) removal from reservoir 1 via runoff or mixing of nearly all of the antecedent rainfall or (2) that streamflow at 27 hours had a 42% contribution from current rainfall. Because there are no measurements to corroborate this observation, we have excluded it from the analysis in order to examine hydrograph separation with realistic initial conditions.

Initial Reservoir Compositions

The isotopic composition of the stream at the beginning of the storm was $\delta^{18}O = -9.68\%$ SMOW. We assumed this value for the prestorm subsurface water in the near-stream surface-saturated zone (C_2) and in the upslope zone (C_3). There is no evidence to suggest that prestorm water was present on the surface of saturated areas. However, we were unable to match the stream isotopic composition unless we included a small amount of preevent water in the surface reservoir. The last rainfall before the June 12 storm occurred on June 6; the total rainfall was 2.4 mm and it had $\delta^{18}O$ of −5.13‰ SMOW. Accordingly, we assumed an initial isotopic composition (C_1) of water on surface-saturated areas (reservoir 1) of −5.1‰ (permissible range −5.0 to −5.5‰). The assumed initial size of reservoir 1 is equivalent to 2.4 mm H_2O over an area equal to 2.2% of the catchment,

although the saturated area was assumed to be 0.5% of the catchment. The initial water in reservoir 1 is enriched in ^{18}O relative to reservoir 2, perhaps by evaporation. The water may, in fact, reside in the soil just below the ground surface (i.e., in reservoir 2), but the model treats this as if it were in reservoir 1 and mixes isotopically with rainfall.

Initial Reservoir Sizes

The reservoir sizes (M_i, $i = 1, 2, 3$) are expressed in units of H_2O mass relative to the total catchment area. Because the surface-saturated area fraction is a model variable and because the water storage capacity is assumed to be a nonlinear function of the saturated area fraction a_s, use of scaling parameters facilitates comparison of the different initial conditions used in this study. The initial size ($M_1(0)$) of reservoir 1 is scaled relative to that of reservoir 2 ($M_2(0)$), which may be obtained directly from (17) using $a_s(0)$. The initial size of reservoir 3 ($M_3(0)$) is scaled relative to the total water storage capacity (at saturation) of reservoir 3 at $t = 0$, which is

$$M_3(\text{sat}) = \rho \phi D (1 - a_s^n(t)) \tag{21}$$

The hydrograph separation is sensitive to the initial size of M_3. If $M_3(0)$ is too small, it is not possible to match the model stream compositions to measurements on the recession limb. We found that if the initial $M_3(0)/M_3(\text{sat})$ is too small, recharge of the near-stream surface-saturated zone (reservoir 2) from mixed preevent water and storm precipitation in reservoir 3 causes the isotopic composition of reservoir 2 to deviate too far from that of the stream during recession. Accordingly, a good hydrograph separation requires a long series of isotopic measurements on the recession limb and a good estimate of $M_3(0)$.

Catchment Water Storage Capacity Relation

The parameters ϕ, D, and n in the catchment water storage capacity relation (17) are unknown. We assumed $n = 0.8$ in order to force the marginal water storage capacity (18) in the catchment to decrease moderately with increasing a_s. We obtained separations with low rms errors (<0.015 $\delta^{18}O$) for values of (ϕD) between 0.30 and 0.45 m. The stream composition errors increase with values outside this range. Accordingly, we assumed $\phi D = 0.3$ m and $n = 0.8$ for most separations. The use of these parameter values makes the marginal water storage capacity in the near-stream saturated zone a factor of 2 larger than the catchment mean when $a_s = 0.03$.

Surface-Saturated Area–Stream Discharge Relations

The parameters a_0 and k in the assumed linear relation between surface-saturated area and stream discharge (19) were varied over a wide range (Table 2). Good mathematical solutions can be obtained for a_0 between 0.005 and 0.065 and k between 60 and 100 m^{-1} h. For fixed values of a_0 and k, the error of fit depends minimally on the initial size (M_3) of reservoir 3, the upslope unsaturated reservoir. The surface-saturated area–stream discharge relation should be obtained from independent field observations. We assumed that $a_0 = 0.005$ and $k = 60$ m^{-1} h.

A Representative Hydrograph Separation

We varied the catchment parameters and initial conditions to find solutions which match the stream isotopic composi-

Table 2. Catchment Parameters and Initial Conditions for Hydrograph Separations of the Gårdsjön F1 A Rainfall Event

Parameter	Description	Equation	Model Values	Estimated Range	Units
	Catchment Parameters				
ϕD	soil porosity times depth	(17)	0.30	0.15–0.45	m
n	exponent in water storage capacity relation	(17)	0.8	0.75–0.85	none
a_0	$a_s(Q_r = 0)$	(19)	0.005	≥ 0.005	none
k	$\partial a_s / \partial Q_r$	(19)	60	0–100	m^{-1} h
	Initial Reservoir Sizes				
$M_1(0)/M_2(0)$	ratio of initial size of water reservoir 1 to water reservoir 2	(4)	0.0125	0.011–0.013	none
$M_2(0)$	initial water in near-stream saturated zone	(17), (7)	calculated		$kg\ m^{-2}$
$M_3(0)/M_3(\text{sat})$	initial upslope zone water relative to capacity	(13)	0.65	≥ 0.65	none
	Initial Isotopic Compositions				
$C_1(0)$	initial $\delta^{18}O$ of M_1	(6)	−5.10	−5 to −5.5	per mil SMOW
$C_2(0)$	initial $\delta^{18}O$ of M_2	(12)	−9.68	−9.68	per mil SMOW
$C_3(0)$	initial $\delta^{18}O$ of M_3	(15)	−9.68	−9.68	per mil SMOW
$C_r(0)$	initial $\delta^{18}O$ of runoff	(3)	−9.68	−9.68	per mil SMOW

tion with an rms error of less than 0.01‰ $\delta^{18}O$. The algorithm performed automated analysis using a test suite with more than 50,000 parameter combinations. Then, we inspected graphs of diagnostic variables for a small subset of cases representing a range of values (see Table 3). The solution illustrated in Figures 3–8 is based on the parameters and initial conditions in Table 2.

The F1 A storm lasted from about 1200 on June 12 to 2300 on June 13, with some very small additional rainfall during the next 12 hours. Peak streamflow near 2400 on June 13 (Figure 5, 48 hours elapsed time) occurs at the same time as the rapid decrease in precipitation intensity (Figure 2), but generally lags the peak precipitation intensity. The observed isotopic composition ($\delta^{18}O$) of precipitation varied from −8‰ to about −20‰ (Figure 2). The calculated isotopic compositions of the reservoirs (Figure 6) and the stream (Figure 3) vary in a complex manner, due to changes in rainfall rate (Figure 2), the isotopic composition of rain (Figure 2), the surface-saturated area (Figure 5), and the reservoir sizes (Figure 7). The isotopic composition of reservoir 1 ("new" water) became isotopically heavier due to mixing with rainfall (Figure 6), and decreased to a final value near −15‰ SMOW. Reservoir 2 (near-stream surface-saturated zone) changes composition only by mixing with water from reservoir 3 (upslope zone) due to replenishment and increase of surface-saturated area. Accordingly, the composition of reservoir 2 is always intermediate between its initial composition ($C_2(0)$) and the evolving composition of reservoir 3 ($C_3(t)$). Reservoir 3 (upslope zone) changes composition by mixing with new precipitation and by mixing with water transferred from reservoir 2 when the surface-saturated area is decreasing. The total shift in isotopic composition of reservoir 3 is governed by the relative sizes and compositions of reservoir 3 and total precipitation.

The isotopic composition of the stream was identical to that of the three reservoirs briefly at one point (see Figure 6, elapsed time about 35 hours). For this condition the algorithm selects the smallest value of f_1 (here, zero) required to match the measured stream composition as shown in Figure 3. At this time the total streamflow was low (Figure 5), and the errors in reservoir sizes and isotopic compositions which this approximation caused are assumed to be small.

At all times the isotopic composition of the stream (Figures 4 and 6) deviates from its initial composition toward the isotopic composition of reservoir 1 (direct precipitation on saturated areas). When the isotopic composition of the stream is between the compositions of reservoirs 1 and 3 (Figure 6, elapsed time near 34 hours), the stream composition is displaced from its initial value toward the composition of reservoir 1. This evidence supports the idea that the streamflow isotopic response from overland flow is more important than that from either the upslope zone (reservoir 3) or from channel precipitation. Finally, the composition of the stream approaches that of reservoir 2 on the recession limb of the hydrograph, as the contribution of surface water from reservoir 1 ceases. The inferred mass fraction of surface water in stream runoff has several peaks (Figure 8). The estimated precision of the solution is about ±0.03 for all times except around 35 hours elapsed time, when C_1 and C_2 are nearly identical. The peak heights and shapes depend on the measured stream compositions as well as on the assumed catchment parameters and initial conditions. The peaks in Figure 8 may be correlated temporally with successive peaks in the antecedent precipitation intensity (Figure 2). All peaks in the overland flow contribution to streamflow occur on the rising limb of the hydrograph. The amount of water held in the catchment reservoirs (Figure 7) varies with time. The near-stream surface-saturated reservoir (M_2) increases from an initial value of 4.33 kg m^{-2} per catchment area, reaches a maximum of 15.3 kg m^{-2} when the surface-saturated area (Figure 5) reaches its maximum, and then declines to 8.5 kg m^{-2} at the end of the simulation. The surface-saturated area varied from about 0.5% to almost 3% of the catchment. The direct precipitation on surface-saturated areas (M_1) increases from an initial value of 0.054 kg m^{-2}, reaches a maximum of 0.366 kg m^{-2} near the end of the rainfall event,

Table 3. Model Sensitivity to Parameter Values and Initial Conditions as Measured by rms Errors in Stream Composition and rms Deviations

Catchment Parameters				Initial Conditions			Deviation
a_0*	k†	ϕD‡	n§	M_3/M_3(sat)‖	M_1/M_2¶	C_1**	(C_r)††
*Parameter a_0 in Surface-Saturated Area–Stream Discharge Relation (19)*
0.001	60	0.30	0.80	0.65	0.0125	-5.2	0.17
0.002	60	0.30	0.80	0.65	0.0125	-5.2	0.044
0.003	60	0.30	0.80	0.65	0.0125	-5.2	0.137
0.004	60	0.30	0.80	0.65	0.0125	-5.2	1.404
0.005	60	0.30	0.80	0.65	0.0125	-5.2	0.009
0.006	60	0.30	0.80	0.65	0.0125	-5.2	0.034
0.007	60	0.30	0.80	0.65	0.0125	-5.2	0.0100
0.008	60	0.30	0.80	0.65	0.0125	-5.2	0.0102
0.009	60	0.30	0.80	0.65	0.0125	-5.2	0.0105
0.010	60	0.30	0.80	0.65	0.0125	-5.2	0.0106
0.011	60	0.30	0.80	0.65	0.0125	-5.2	0.0115
0.012	60	0.30	0.80	0.65	0.0125	-5.2	0.0119
0.013	60	0.30	0.80	0.65	0.0125	-5.2	0.0123
0.014	60	0.30	0.80	0.65	0.0125	-5.2	0.0124
0.015	60	0.30	0.80	0.65	0.0125	-5.2	0.0107
0.016	60	0.30	0.80	0.65	0.0125	-5.2	0.0108
0.017	60	0.30	0.80	0.65	0.0125	-5.2	0.0109
0.018	60	0.30	0.80	0.65	0.0125	-5.2	0.0109
0.019	60	0.30	0.80	0.65	0.0125	-5.2	0.0110
0.020	60	0.30	0.80	0.65	0.0125	-5.2	0.0111
*Parameter k in Surface-Saturated Area–Stream Discharge Relation (19)*
0.005	20	0.30	0.80	0.65	0.0125	-5.2	0.25
0.005	25	0.30	0.80	0.65	0.0125	-5.2	1.71
0.005	30	0.30	0.80	0.65	0.0125	-5.2	0.19
0.005	35	0.30	0.80	0.65	0.0125	-5.2	1.67
0.005	40	0.30	0.80	0.65	0.0125	-5.2	1.60
0.005	45	0.30	0.80	0.65	0.0125	-5.2	1.42
0.005	50	0.30	0.80	0.65	0.0125	-5.2	0.62
0.005	55	0.30	0.80	0.65	0.0125	-5.2	1.04
0.005	60	0.30	0.80	0.65	0.0125	-5.2	0.0091
0.005	65	0.30	0.80	0.65	0.0125	-5.2	0.074
0.005	70	0.30	0.80	0.65	0.0125	-5.2	0.0091
0.005	75	0.30	0.80	0.65	0.0125	-5.2	0.0092
0.005	80	0.30	0.80	0.65	0.0125	-5.2	0.0092
0.005	85	0.30	0.80	0.65	0.0125	-5.2	0.0092
0.005	90	0.30	0.80	0.65	0.0125	-5.2	0.0092
0.005	95	0.30	0.80	0.65	0.0125	-5.2	0.0092
0.005	100	0.30	0.80	0.65	0.0125	-5.2	0.0112
*Parameter (ϕD) in Catchment Water Storage Capacity Relation (17)*
0.005	60	0.10	0.80	0.65	0.0125	-5.2	2.09
0.005	60	0.15	0.80	0.65	0.0125	-5.2	2.08
0.005	60	0.20	0.80	0.65	0.0125	-5.2	2.03
0.005	60	0.25	0.80	0.65	0.0125	-5.2	0.15
0.005	60	0.30	0.80	0.65	0.0125	-5.2	0.009
0.005	60	0.35	0.80	0.65	0.0125	-5.2	0.012
0.005	60	0.40	0.80	0.65	0.0125	-5.2	0.013
0.005	60	0.45	0.80	0.65	0.0125	-5.2	0.015
0.005	60	0.50	0.80	0.65	0.0125	-5.2	0.045
*Parameter n in Catchment Water Storage Capacity Relation (17)*
0.005	60	0.30	0.70	0.650	0.0125	-5.2	0.046
0.005	60	0.30	0.75	0.650	0.0125	-5.2	0.013
0.005	60	0.30	0.80	0.650	0.0125	-5.2	0.009
0.005	60	0.30	0.85	0.650	0.0125	-5.2	1.75
0.005	60	0.30	0.90	0.650	0.0125	-5.2	2.08
*Initial Mass of Water in Upslope Nonsaturated Zone Reservoir $(M_3/M_3(sat))$*
0.005	60	0.30	0.80	0.40	0.0125	-5.2	1.97
0.005	60	0.30	0.80	0.45	0.0125	-5.2	1.50
0.005	60	0.30	0.80	0.50	0.0125	-5.2	0.17
0.005	60	0.30	0.80	0.55	0.0125	-5.2	1.67
0.005	60	0.30	0.80	0.60	0.0125	-5.2	1.38
0.005	60	0.30	0.80	0.65	0.0125	-5.2	0.009
0.005	60	0.30	0.80	0.70	0.0125	-5.2	0.018
0.005	60	0.30	0.80	0.75	0.0125	-5.2	0.009

Table 3. (continued)

Catchment Parameters				Initial Conditions			Deviation
a_0*	k†	ϕD‡	n§	M_3/M_3(sat)‖	M_1/M_2¶	C_1**	(C_r)††
				$M_1(0)/M_2(0)$‡‡			
0.005	60	0.30	0.80	0.650	0.0025	−5.2	0.57
0.005	60	0.30	0.80	0.650	0.0050	−5.2	0.18
0.005	60	0.30	0.80	0.650	0.0075	−5.2	0.015
0.005	60	0.30	0.80	0.650	0.0100	−5.2	0.12
0.005	60	0.30	0.80	0.650	0.0125	−5.2	0.009
0.005	60	0.30	0.80	0.650	0.0150	−5.2	0.94
0.005	60	0.30	0.80	0.650	0.0175	−5.2	1.12
0.005	60	0.30	0.80	0.650	0.0200	−5.2	0.18
0.005	60	0.30	0.80	0.650	0.0225	−5.2	0.29
			Initial Oxygen Isotope Composition C_1 of Water in Reservoir 1				
0.005	60	0.30	0.80	0.65	0.0125	−4.5	0.94
0.005	60	0.30	0.80	0.65	0.0125	−4.6	0.94
0.005	60	0.30	0.80	0.65	0.0125	−4.7	0.94
0.005	60	0.30	0.80	0.65	0.0125	−4.8	0.94
0.005	60	0.30	0.80	0.65	0.0125	−4.9	0.04
0.005	60	0.30	0.80	0.65	0.0125	−5.0	0.009
0.005	60	0.30	0.80	0.65	0.0125	−5.1	0.009
0.005	60	0.30	0.80	0.65	0.0125	−5.2	0.009
0.005	60	0.30	0.80	0.65	0.0125	−5.3	0.009
0.005	60	0.30	0.80	0.65	0.0125	−5.4	0.009
0.005	60	0.30	0.80	0.65	0.0125	−5.5	0.009
0.005	60	0.30	0.80	0.65	0.0125	−5.6	0.12
0.005	60	0.30	0.80	0.65	0.0125	−5.7	0.12
0.005	60	0.30	0.80	0.65	0.0125	−5.8	0.12
0.005	60	0.30	0.80	0.65	0.0125	−5.9	0.12

*The parameters a_0 and k determine via equation (19) and $Q_r(0)$ the initial surface-saturated area fraction.
†Slope of surface-saturated area fraction versus catchment streamflow (units m^{-1} h).
‡Catchment mean water storage capacity in units of water depth (meters).
§Power law exponent in the catchment water storage capacity function (17) which defines the water storage capacity distribution within the catchment.
‖Relative saturation (0 to 1) of the upslope non-surface-saturated zone (reservoir 3) at the start of the simulation.
¶Initial size of reservoir 1 as a fraction of the initial water stored in reservoir 2 (near-stream surface-saturated zone).
**Initial isotopic composition (in per mil $\delta^{18}O$) of reservoir 1.
††Root mean square deviation (in per mil $\delta^{18}O$) of model stream compositions from measured values for all measurements.
‡‡Initial reservoir mass for direct precipitation on surface-saturated areas as fraction of initial mass in near-stream surface-saturated zone.

somewhat earlier than M_2 (Figure 7), and then declines to 0.197 kg m^{-2}. The upslope zone increases from an initial value near 192 kg m^{-2} to a maximum of 239 kg m^{-2} at the end of the simulation. The total amount of subsurface water held in the catchment at the end of the simulations is about 239 (M_3) + 8.5 (M_2) = 247.5 kg m^{-2}, which is very wet, but well below the assumed catchment storage capacity of 300 kg m^{-2}. The inferred lower bound on reservoir size (greater than 300 kg m^{-2}) is smaller than the storage capacity estimated by modeling the ^{18}O flow through this catchment over a 3-year period by *Lindström and Rodhe* [1986]. Using a modified version of the HBV-PULSE model for catchment runoff [*Bergström*, 1992], they obtained a reservoir volume of about 400 kg m^{-2}. However, the two results are not discrepant at this time because the storage capacity estimated in the present paper is a lower bound.

Do the Solutions Have a Particular Shape?

The mathematical solutions $f_1(t)$ to the mass balance equations for hydrograph separation might have a particular shape which describes how overland flow in the catchment responds to rainfall or snowmelt forcing under various conditions. For example, one might expect the mass fraction of surface water in the stream runoff $(f_1(t))$ to be propor-

tional to antecedent values of the precipitation rate and surface-saturated area fraction and inversely proportional to a residence time for precipitation on surface-saturated areas of the catchment. Such an approach is generally consistent with the variable source area hypothesis of streamflow generation [*Hewlett and Hibbert*, 1967], which is central to our stream hydrograph separation method. We describe a function (22) for estimating the fraction of streamflow generated by overland flow. The input variables for the function include antecedent values of the rainfall intensity, surface-saturated area fraction, and streamflow and a characteristic time for catchment response. The antecedent time argument is a function of time elapsed after onset of rainfall.

Many of the purely mathematical solutions with low rms errors can be represented with the surface water fraction $f_1(t)$ given by a function of the following form:

$$f_1(t > t_0) = f_1(t_0) + \frac{a_s(t - \hat{t})Q_p(t - \hat{t})}{Q_r(t - \hat{t})} \frac{\hat{t}}{\tau} \quad (22)$$

where

$$\hat{t} \text{ (hours)} = k_1(t - t_0) \quad (23)$$

Equations (22) and (23) are valid only for $t \geq t_0$ where t_0 is the time at which rainfall begins (12 hours). The term $\hat{t}$ is the
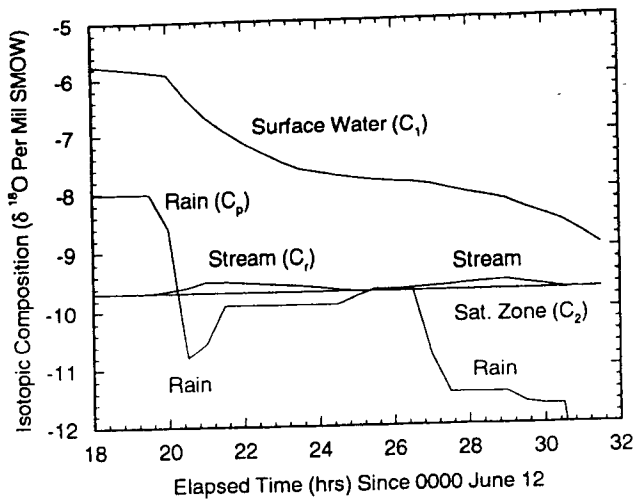
Figure 4. Oxygen isotopic compositions of the stream (C_r), rain (C_p), surface water (C_1), and the near-stream saturated zone (C_2) for elapsed times from 18 to 32 hours. The stream isotopic response to the first two rainfall peaks (Figure 2) is a shift away from the composition of the rain and toward that of surface water (direct precipitation on saturated areas).

variable lag time of peak streamflow response to direct precipitation on surface-saturated areas. The values of the parameters k_1 (0.115 h^{-1} h^{-1}) and τ (7.5 hours) for the case illustrated in Figures 3–8 were obtained by matching peaks using the stream hydrograph separation results. The constant k_1 determines how much the successive peaks in overland flow contributions to streamflow are stretched relative to successive peaks in the precipitation rate forcing term. The term τ is a residence time for "new" water in saturated areas. We solved for k_1 by visually matching relative maxima of $f_1(t)$ inferred from the hydrograph separation method with relative maxima of $f_1(t)$ given by (22). We solved for τ by matching relative peak heights for $f_1(t)$ based on the hydrograph separation equations and (22). The antecedent streamflow, rather than streamflow at time t, is a measure of antecedent wetness and subsurface water fluxes in the catchment. Qualitatively, as the catchment gets wetter
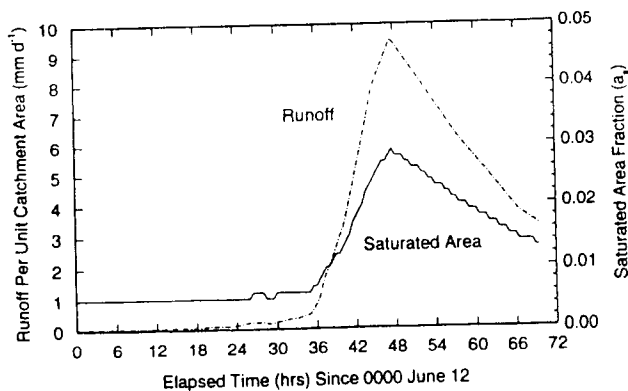

Figure 5. Stream runoff per unit catchment area (in millimeters per day) [after *Rodhe*, 1987] and model value (this paper) of surface-saturated area fraction (a_s) during the Gårdsjön F1 A rain event.
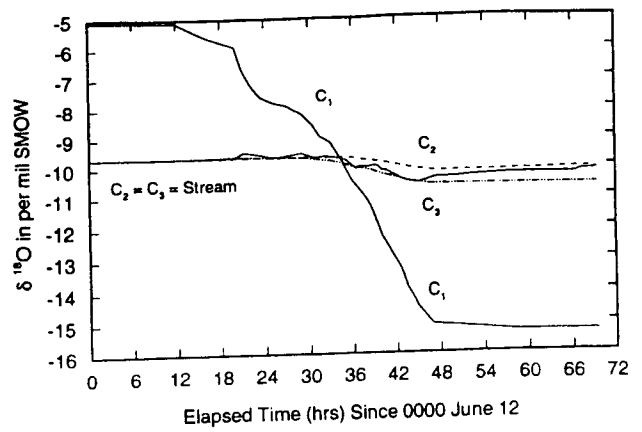

Figure 6. Oxygen isotopic compositions of reservoirs and stream runoff during the Gårdsjön F1 A rain event. The lines labeled C_1 (solid), C_2 (dashed), and C_3 (dashed with double dots) are the modeled oxygen isotopic compositions of reservoir 1 (direct precipitation on saturated areas), of reservoir 2 (near-stream saturated zone), and of reservoir 3 (upslope zone). The solid line near the lines labeled C_2 and C_3 is the isotopic composition of the stream interpolated from measured values.

and as the total streamflow increases, a larger antecedent precipitation rate and/or a greater saturated area fraction is required to generate the same fraction of streamflow via overland flow. The fraction of streamflow $f_1(t_0)$ which results from direct precipitation on saturated areas at the onset of the storm must be added to adjust for the initial state. This value (0 for the case in Figures 3–8) was obtained by solving the stream hydrograph separation equations, which vary with model parameters and initial conditions.

The overland flow contributions to streamflow estimated by (22) match the estimates based on the hydrograph separation for the rising limb of the hydrograph (Figure 8). The root mean square of the difference in $f_1(t)$ for t between 34 and 48 hours is 0.03. The close agreement is shown in Figure
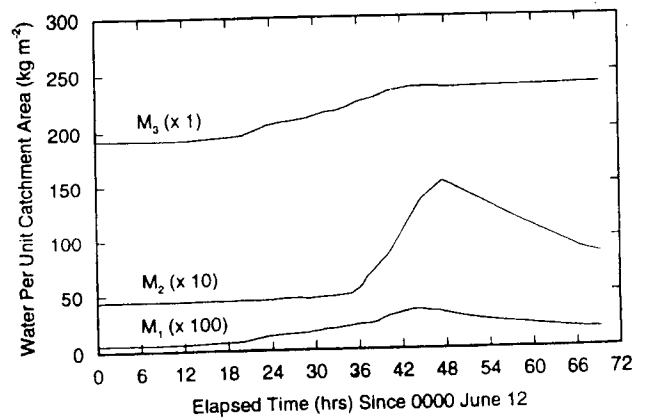

Figure 7. Water storage in model water reservoirs during the Gårdsjön F1 A rainfall-runoff event. The lines labeled M_1, M_2, and M_3 are the model sizes of reservoir 1 (direct precipitation on surface-saturated areas), of reservoir 2 (near-stream saturated zone), and of reservoir 3 (upslope areas). The values are normalized to the entire catchment area.

9. However, the early rainfall made only a small contribution to streamflow (Figure 8), despite the fact that rainfall rates were relatively high (Figure 2) when streamflow was low (Figure 5).

The fraction of "new" water contributing to flow during recession is uncertain, but the hydrograph separation results suggest the fraction is between zero and a few percent. Therefore we do not ascribe any significance to the differences between the results obtained by hydrograph separation and those estimated from (22) for the tail region of Figure 8. Much more work is needed to assess whether (22) can be used for different conditions to estimate the mass fraction of streamflow generated by overland flow. If so, then isotopic methods might be used to assess the overland flow response of a catchment to rainfall events.

The proposed overland flow predictor function (22) guarantees neither a unique solution nor a correct solution. However, it ensures that the selected solutions have overland flow contributions to streamflow which (1) vary with antecedent precipitation intensity and catchment wetness and (2) tend toward zero at long times.

Figure 9. Fraction of streamflow from direct precipitation on surface-saturated areas ("surface water") estimated by (22) versus the fraction inferred from hydrograph separation for elapsed times between 35 and 50 hours.

Conclusions

The variable source area hydrograph separation method provides a new approach to runoff source modeling using stable isotopes. The variable source area hydrograph separation method explicitly conserves water and tracer. It assumes continuous open system isotope mixing, which is a more realistic description of catchment processes than "batch"-mixing models. The quality of hydrograph separations obtained by using different parameter values can be compared objectively by the rms deviations of model stream isotopic compositions from measured values and by whether the resulting solutions violate any hydrologic criteria.

This hydrograph separation method can be used in catchment studies for three applications: (1) to estimate the water storage capacity, to estimate the overland flow response to rainfall, and to infer relations between saturated area and streamflow; (2) to test the hydrograph separation method; and (3) to test the variable source area hypothesis of stream-
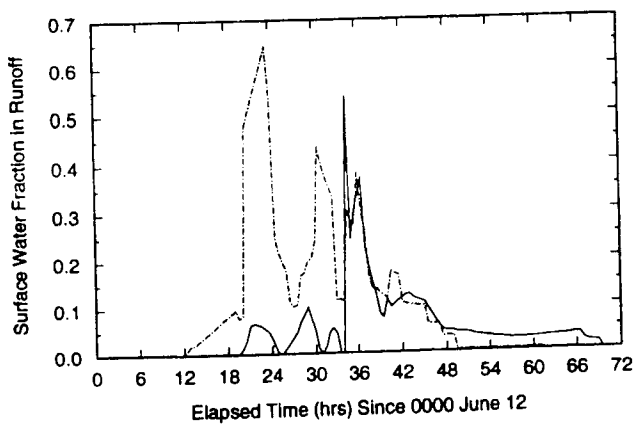
flow generation. Use of the hydrograph separation method for any of these applications requires implicit assumptions or knowledge derived from the other two applications. We used the hydrograph separation method in application 1 and assumed the validity of both the hydrograph separation method and the variable source area hypothesis for the Gårdsjön F1 A catchment and rainfall event.

The hydrograph separation results are sensitive to the assumed relations among surface-saturated area fraction, stream runoff, and catchment water storage capacity. This allows detailed isotopic measurements to be used to estimate parameters useful in lumped models of catchment water storage, streamflow generation, and flow path utilization. This approach, however, requires corroborating field measurements and comparison of parameters retrieved using the same model for multiple events on the same catchment.

Perhaps the most interesting result is that relative maxima in the rainfall rate can be resolved in the overland flow contributions to streamflow when the new hydrograph separation method is used. We proposed a simple transfer function which relates the overland flow streamflow response to varying precipitation rates and antecedent conditions. This function closely matches the solution obtained by the hydrograph separation method at times for which the errors of the latter method are smallest. More research is needed before the proposed function (or a similar one) can be used in any predictive way.

Recommendations for Further Study

We emphasize that this hydrograph separation method has not been tested in the strict sense. Therefore an important prerequisite is a scientific test, which requires application of the hydrograph separation model to isotopic data from a catchment where (1) the relation between saturated area and streamflow is accurately known, (2) the catchment water storage capacity and its distribution in the catchment are well established, and (3) the initial and final reservoir sizes and their isotopic compositions are well known. A formal test of the separation method should not be based on comparison with the time-dependent streamflow contribu-

Figure 8. Inferred mass fraction of runoff contributed by direct precipitation on surface-saturated areas (i.e., $f_1(t)$) during the Gårdsjön F1 A rain event (solid line). The dashed-dotted line represents the value of $f_1(t)$ calculated from (22).
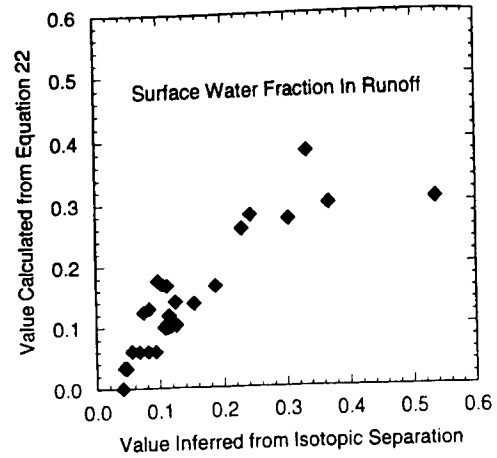
tion from overland flow because there is no method for obtaining this quantity without relying on yet another model. Instead, the hydrograph separation method must be evaluated using its capability to correctly retrieve the state variables (initial and final reservoir sizes and isotopic compositions), catchment water storage capacity, and relations between streamflow and saturated area. The capability of the hydrograph separation method to correctly retrieve a single parameter can be assessed by using measured values of other parameters as constants in the separation algorithm and then using a variation of parameter method to estimate one unknown parameter, and then comparing it to the measured value. In all cases, it is necessary to estimate the precision (applicable at the catchment scale) for all parameters. An overall error budget and analysis are recommended before testing the hydrograph separation method using new field data. We recommend a maximum sampling interval of 15 minutes for rainfall and streamflow with duplicate sampling and analysis. Redundant measurements are required to increase precision, to detect blunders, and to adequately define the peak shapes in the hydrograph separation.

Hydrologic simulations at the catchment scale using lumped and spatially distributed topographically forced hydrologic models [e.g., *Binley and Beven*, 1992] can be further tested by incorporating stable isotope and chemical tracers. The open system isotope mixing approach described here could be incorporated in such models to simulate temporal and spatial changes in isotopic composition of water in catchments and runoff. If such an approach is successful, hydrometric, isotopic, and chemical measurements might be used to validate spatially distributed models [e.g., *Robson et al.*, 1992]. The principal value of such work is in developing the capability to predict catchment behavior, flow path utilization, water quality, and streamflow responses to changing conditions.

Notation

C_i relative isotopic abundance of reservoir i ($i = 1, 2, 3$), per mil.

C_p relative isotopic abundance of precipitation, per mil.

C_r relative isotopic abundance of stream water, per mil.

M_i mass of water (per unit catchment area) in reservoir i, kg m^{-2}.

M_3(sat)   water storage capacity (per unit catchment area) in reservoir 3, kg m^{-2}.

Q_1 water flux from reservoir 1 to stream, m h^{-1}.

Q_2 water flux from reservoir 2 to stream, m h^{-1}.

Q_3 water flux from reservoir 3 to reservoir 2, m h^{-1}.

Q_p flux of precipitation to land surface (per unit area), m h^{-1}.

Q_r stream discharge from catchment (per unit area), m h^{-1}.

T_i product $C_i M_i$ ($i = 1, 2, 3$), kg m^{-2} per mil.

a_s surface-saturated area fraction of catchment.

f_1 mass fraction of total runoff from reservoir 1.

f_2 mass fraction of total runoff from reservoir 2.

a_0 constant in a_s-Q_r relation (equation (19)).

k constant in a_s-Q_r relation (equation (19)), m^{-1} h.

k_1 coefficient in (23), h h^{-1}.

n constant in water storage capacity relation (equation (17)).

t time, hours.

$\hat{t}$ variable lag time of streamflow response to precipitation (see equation (23)), hours.

ρ water density, kg m^{-3}.

D soil depth, m.

ϕ effective soil porosity.

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