

# Comparison of hydrochemical tracers to estimate source contributions to peak flow in a small, forested, headwater catchment

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**Abstract.** Three-component (throughfall, soil water, groundwater) hydrograph separations at peak flow were performed on 10 storms over a 2-year period in a small forested catchment in north-central Maryland using an iterative and an exact solution. Seven pairs of tracers (deuterium and oxygen 18, deuterium and chloride, deuterium and sodium, deuterium and silica, chloride and sodium, and sodium and silica) were used for three-component hydrograph separation for each storm at peak flow to determine whether or not the assumptions of hydrograph separation routinely can be met, to assess the adequacy of some commonly used tracers, to identify patterns in hydrograph-separation results, and to develop conceptual models for the patterns observed. Results of the three-component separations were not always physically meaningful, suggesting that assumptions of hydrograph separation had been violated. Uncertainties in solutions to equations for hydrograph separations were large, partly as a result of violations of assumptions used in deriving the separation equations and partly as a result of improper identification of chemical compositions of end-members. Results of three-component separations using commonly used tracers were widely variable. Consistent patterns in the amount of subsurface water contributing to peak flow (45–100%) were observed, no matter which separation method or combination of tracers was used. A general conceptual model for the sequence of contributions from the three end-members could be developed for 9 of the 10 storms. Overall results indicated that hydrochemical and hydrometric measurements need to be coupled in order to perform meaningful hydrograph separations.

## 1. Introduction

During the past several decades, controversy over the mechanisms and sources of storm flow in small catchments around the world has generated a number of field studies and a large amount of literature. Storm flow hydrograph separations have evolved from two components (precipitation and groundwater) to three components (precipitation, soil water, and groundwater) as the importance of soil-water contributions to storm flow has been recognized. Along with three-component separations came the requirement of more tracers, and the use of combined isotopic and chemical tracers became common.

In the mid-1970s, researchers of catchment hydrological processes began using natural tracers to separate storm flow hydrographs into time-source (prestorm and storm) components [Fritz *et al.*, 1974; Mook *et al.*, 1974; Sklash *et al.*, 1976]. The early studies usually concluded that groundwater (assumed equivalent to prestorm water) contributions to storm flow were large, that is, equal to or greater than 50% of the total storm flow. Martinec [1975], Fritz *et al.* [1976], and Bottomley *et al.* [1984] found that groundwater plus minor amounts of soil water could explain the isotopic composition of

storm flow. Sklash and Farvolden [1979] used isotopic and specific conductance data collected from two small catchments in Quebec, Canada, to separate storm flow into groundwater and overland-flow components. Although Sklash and Farvolden [1979] sampled soil water, they assumed it was a negligible component of storm flow and concluded that groundwater was the most significant component. In contrast to the 1970 and early 1980 studies, Kennedy *et al.* [1986] concluded that soil water must be a significant contributor to storm flow in the Mattole River Basin in northwestern California. Sklash *et al.* [1986], in a study of chemical and isotopic tracers in the Maimai catchments in New Zealand, concluded that because of the nonconservative behavior of total dissolved solids (as indicated by specific conductance) and chloride ( $\text{Cl}^-$ ), conservative isotopic tracers are useful in interpreting variations in chemistry. Turner *et al.* [1987] used deuterium (D), oxygen 18 ( $^{18}\text{O}$ ), and  $\text{Cl}^-$  concentrations as tracers in the Salmon catchment in Western Australia and found that for three different storms, 60–95% of storm flow was prestorm water. Except for that of Kennedy *et al.* [1986], studies before the late 1980s had either dismissed soil water as an insignificant component of storm flow or had added it in with groundwater as a source. DeWalle *et al.* [1988] found that a two-component model of storm flow separation was inadequate to explain isotopic variations in storm flow at the Fish Run catchment in southwestern

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Pennsylvania. They used  $^{18}\text{O}$  as a tracer in a three-component model of storm flow separation and concluded that soil water, collected by tension lysimeters, accounted for 12–31% of peak storm flow. *Swistock et al.* [1989] further emphasized the importance of soil water as a component of storm flow in the Fish Run catchment. In a steep headwater catchment in Virginia, *Bazemore et al.* [1994] found that pre-event soil water contributed 50–65% of peak storm flow.

Storm flow separations using two tracers and three components can be calculated by use of a mass balance approach and the simultaneous solution of three equations and three unknowns:

$$Q_{\text{ST}} = Q_{\text{TF}} + Q_{\text{SW}} + Q_{\text{GW}} \quad (1)$$

$$C1_{\text{ST}}Q_{\text{ST}} = C1_{\text{TF}}Q_{\text{TF}} + C1_{\text{SW}}Q_{\text{SW}} + C1_{\text{GW}}Q_{\text{GW}} \quad (2)$$

$$C2_{\text{ST}}Q_{\text{ST}} = C2_{\text{TF}}Q_{\text{TF}} + C2_{\text{SW}}Q_{\text{SW}} + C2_{\text{GW}}Q_{\text{GW}}, \quad (3)$$

where  $Q$  is discharge,  $C1$  is concentration of tracer 1,  $C2$  is concentration of tracer 2, and the subscripts ST, TF, SW, and GW refer to stream, throughfall, soil water, and groundwater, respectively.

To verify the accuracy of the calculated fractions of components contributing to storm flow, one can perform multiple hydrograph separations on the same storm using different pairs of tracers and compare the results. If the results of all of the hydrograph separations compare well, one might become convinced that the hydrograph-separation technique is an adequate tool to use in catchment hydrology and that the tracers selected behaved appropriately. In contrast, disparate results among the hydrograph separations would suggest that either (1) there is a problem with the hydrograph-separation technique (i.e., one or more of the assumptions of hydrograph separation were violated, e.g., one or more of the tracers behaved nonconservatively), (2) sampling error occurred (i.e., one or more of the three components was not adequately chemically characterized), or (3) the data for the storm were not suitable for hydrograph separation (i.e., the concentrations of the tracers for at least one of the components were too similar to the concentrations of the tracers in one of the other components).

Other useful approaches that can be used to examine stream water chemistry and identify source components include end-member mixing analysis (EMMA) [*Christophersen et al.*, 1990; *Hooper et al.*, 1990] and principal components analysis (PCA). EMMA is an analytical approach for solving a set of overdetermined equations. It is a useful technique for assessing whether appropriate end-members have been chosen for a storm and for assessing the conservativity of a pair of tracers. PCA is a standard multivariate data-analysis technique that can be applied to stream water data to determine the number of source solutions and their chemical signature [*Christophersen and Hooper*, 1992]. Despite the mathematical sophistication available, three-component hydrograph separations typically are done using pairs of tracers. Results presented in this paper demonstrate that the use of pairs of tracers to perform hydrograph separations may not be sufficient to identify all source components.

The purpose of this paper is to compare three-component hydrograph separations at peak flow using seven pairs of five different tracers ( $\delta\text{D}$  and  $\delta^{18}\text{O}$ ,  $\delta\text{D}$  and  $\text{Cl}^-$ ,  $\delta\text{D}$  and sodium ( $\text{Na}^+$ ),  $\delta\text{D}$  and silica ( $\text{SiO}_2$ ),  $\text{Cl}^-$  and  $\text{SiO}_2$ ,  $\text{Cl}^-$  and  $\text{Na}^+$ , and  $\text{Na}^+$  and  $\text{SiO}_2$ ) for a set of 10 storms, collected over

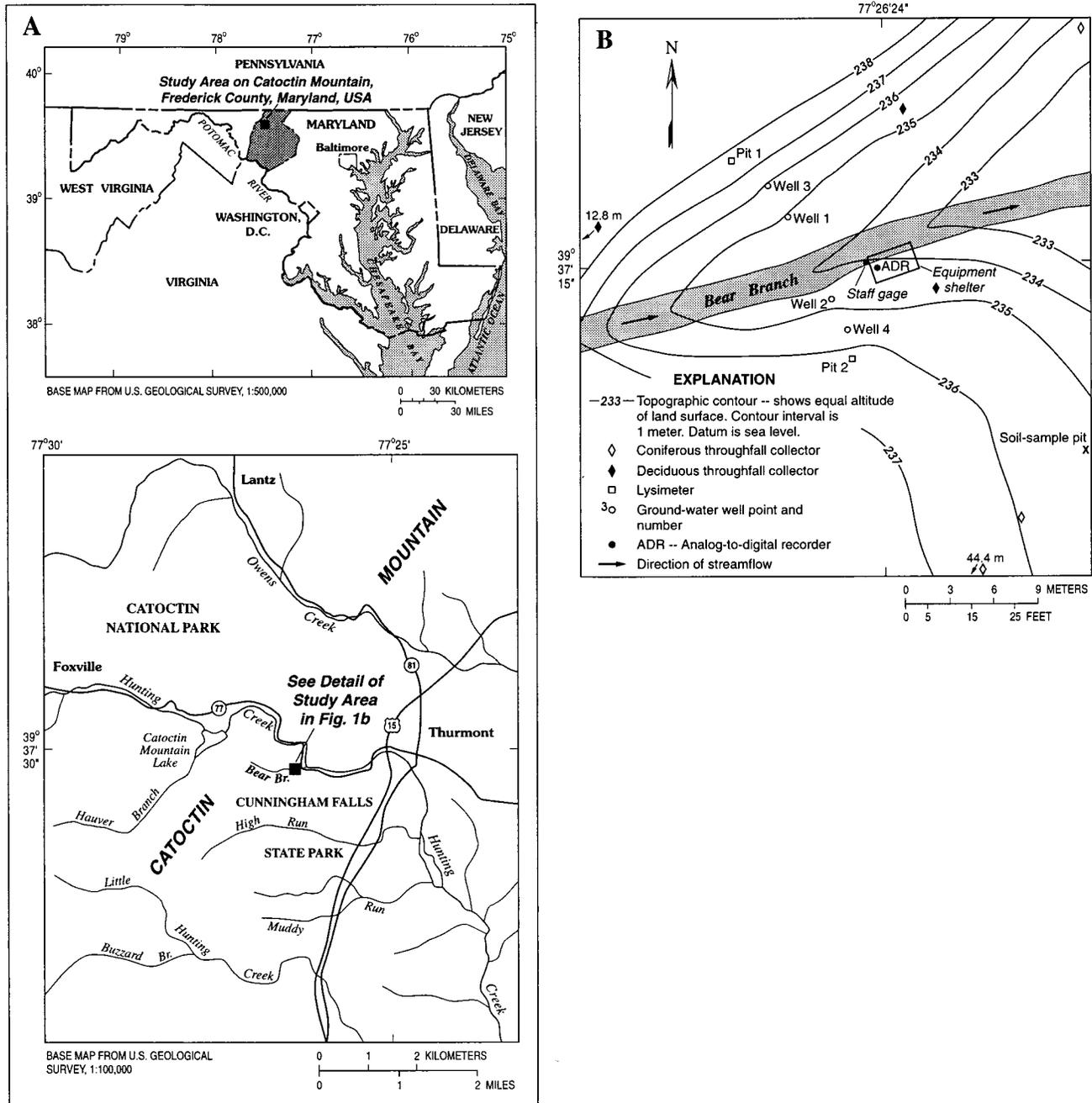
a 2-year period in one small forested catchment. This is the only study known to the authors in which source components at peak flow have been identified for multiple storms, encompassing all seasons, using different pairs of chemical and isotopic tracers on a single catchment. The hydrograph-separation results and analysis allow the following series of questions to be addressed.

1. Can three-component hydrograph separations be performed routinely in this catchment for all storms; that is, are the assumptions underlying the method almost always met?
2. If three-component hydrograph separations can be performed, are consistent quantitative results obtained using different pairs of chemical and isotopic tracers?
3. If three-component hydrograph separations can be performed, are consistent patterns in the results observed? For example, by examining component mixing diagrams, is a 50% groundwater contribution at the peak of the hydrograph for all tracers across all seasons observed?
4. If three-component hydrograph separations can be performed, can a reasonable conceptual model be developed for the observed patterns in the results?

In order to answer these questions, hydrograph separations at peak flow were performed on 10 storms in the same catchment using seven pairs of tracers that commonly have been used in hydrograph separation. Two-dimensional component mixing diagrams were used to interpret the storm data qualitatively and to determine whether or not the storm was suitable for doing a three-component hydrograph separation. In addition, the effect of sampling error on the hydrograph separation results was examined using Monte Carlo simulations. Results of the analysis indicated that (1) hydrograph separations routinely can be performed but that the results may not always be physically meaningful, (2) consistent quantitative results were not obtained from the seven pairs of tracers for any of the storms, (3) consistent patterns in the amount of subsurface water (groundwater and soil water) that contributed to the peak of each hydrograph were observed, (4) a reasonable conceptual model for the sequence of contributions from the three components could be developed and was consistent for 9 of the 10 storms, and (5) incorporation of sampling error into the hydrograph separations generally indicated that large uncertainties exist in calculated hydrograph components.

## 2. Description of Study Area

Bear Branch is a 98-ha catchment in the Blue Ridge Physiographic Province on the eastern flank of Catoctin Mountain in north-central Maryland (Figure 1a). The climate is humid temperate, and in north-central Maryland the long-term (1931–1980) average annual air temperature was  $12^\circ\text{C}$  and average precipitation was 1110 mm [*National Oceanic and Atmospheric Administration*, 1981]. The Bear Branch catchment contains an eastward-flowing perennial headwater stream and is covered by a mature oak-hickory-maple-beech forest (90%), with hemlock trees (10%) near the stream channel. Topography is steep (altitudes range from 233 m at the gauge to 500 m at the ridge crest) and rocky, and average stream gradient is 203 m/km (20%). The catchment is underlain entirely by the lower unit of the Weverton Formation, a quartzite [*Fauth*, 1977]. The soils are Edgemont-Chandler very stony loams (Ultisols and Inceptisols) with 20% to 60% slopes [*Matthews*, 1960].



**Figure 1.** (a) Location of study area on Catoclin Mountain, Maryland. (b) Detailed map of topography and instrumentation sites near the streamflow gauging station in the Bear Branch catchment.

### 3. Methods of Data Collection

Throughfall was collected by a 203-mm-diameter polyethylene funnel approximately 1.2 m above the forest floor, connected to a 1-L brown polyethylene collection bottle by Tygon tubing (any use of trade, product, or firm names is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey). The tubing was looped to limit evaporation of the sample. Three collectors were located beneath the canopies of deciduous trees, and three collectors were located beneath the canopies of coniferous trees (Figure 1b). The three collectors beneath each canopy type were composited at least weekly to yield one deciduous and one coniferous sample. McDonnell *et al.* [1990] found that changes in the

isotopic composition of rain during a storm can have significant effects on hydrograph-separation results. Changing isotopic composition during a storm complicates hydrograph separation because it violates the second assumption outlined by Sklash and Farvolden [1979]. It is possible that the isotopic composition of rain (or throughfall) changes enough during the storm that it becomes too similar in composition to one of the other components for a successful hydrograph separation to be performed. In this study, only total storm rainfall (and throughfall) was collected and analyzed; incrementally weighted samples were not collected, and therefore this effect cannot be analyzed.

Soil water from two depths was collected by zero-tension

**Table 1.** Description of Storm Characteristics and Input Data Used in Hydrograph Separations at Peak Flow

| Tracer           | Fall  |                  |                      | Winter,<br>Dec. 10–12,<br>1992 | Spring              |                   | Summer           |                    |                  |                     |
|------------------|---|------------------|----------------------|--------------------------------|---------------------|-------------------|------------------|--------------------|------------------|---------------------|
|                  | Oct. 23–24,<br>1990   | Sept. 4,<br>1991 | Sept. 18–19,<br>1991 |                                | March 6–10,<br>1992 | April 21,<br>1992 | June 18,<br>1991 | Aug. 9–10,<br>1991 | Aug. 19,<br>1991 | Aug. 18–19,<br>1992 |
|                  | <i>Amount of Precipitation, mm</i>                                    |                  |                      |                                |                     |                   |                  |                    |                  |                     |
|                  | 68.3  | 47.0             | 77.0                 | 85.6                           | 40.9                | 93.0              | 33.8             | 24.6               | 27.9             | 25.9                |
|                  | <i>7-Day Antecedent Precipitation, mm</i>                             |                  |                      |                                |                     |                   |                  |                    |                  |                     |
|                  | 28.7  | 0                | 5.10                 | 5.84                           | 0                   | 5.08              | 19.6             | 1.78               | 2.54             | 26.7                |
|                  | <i>Additional Throughfall in Collectors Before or After Storm, mm</i> |                  |                      |                                |                     |                   |                  |                    |                  |                     |
|                  | 28.7  | 4.60             | 1.30                 | 0                              | 0                   | 3.00              | 19.6             | 0.80               | 2.50             | 0.80                |
|                  | <i>Discharge at Peak of Hydrograph, L/s</i>                           |                  |                      |                                |                     |                   |                  |                    |                  |                     |
|                  | 275   | 27.2             | 28.4                 | 278                            | 65.7                | 533               | 151              | 22.6               | 3.17             | 36.0                |
|                  | <i>Tracer Concentrations in Throughfall</i>                           |                  |                      |                                |                     |                   |                  |                    |                  |                     |
| $\delta D$       | -23   | -28              | -14                  | -76.4                          | -38.5               | -24.5             | -25.5            | -18.5              | -35              | -53                 |
| $\delta^{18}O$   | -5.65   | -5.55            | -3.9                 | -12.2                          | -6.95               | -4.85             | -5.15            | -4.1               | -6.45            | -8.3                |
| Cl               | 28  | 28.2             | 7.64                 | 15.9                           | 10.0                | 14.4              | 32.3             | 24.1               | 28.2             | 6.98                |
| Na               | 19.1  | 9.9              | 2.26                 | 6.74                           | 3.7                 | 9.7               | 6.4              | 5                  | 2.31             | 0.39                |
| SiO <sub>2</sub> | 0.1   | 1                | 0.1                  | 0.1                            | 0                   | 0.1               | 2.2              | 2.8                | 0.1              | 0.1                 |
|                  | <i>Tracer Concentrations in Soil Water</i>                            |                  |                      |                                |                     |                   |                  |                    |                  |                     |
| $\delta D$       | -13.8   | -27.3            | -15.7                | -31.8                          | -60.5               | -41.7             | -29              | -18.7              | -35.8            | -38.5               |
| $\delta^{18}O$   | -3.95   | -5.7             | -4.33                | -6.17                          | -9.5                | -7.05             | -5.75            | -4.07              | -6.48            | -6.35               |
| Cl               | 77.7  | 24.4             | 10.9                 | 28.4                           | 36.2                | 24.9              | 17.2             | 23.2               | 11.2             | 10.1                |
| Na               | 31.3  | 11.8             | 7.56                 | 10.7                           | 16.3                | 15.0              | 9.27             | 7.27               | 4.57             | 5.81                |
| SiO <sub>2</sub> | 7.7   | 7.96             | 12.5                 | 19.0                           | 29                  | 18.7              | 56.1             | 13.7               | 10.7             | 19.5                |
|                  | <i>Tracer Concentrations in Stream Water at Peak of Hydrograph</i>    |                  |                      |                                |                     |                   |                  |                    |                  |                     |
| $\delta D$       | -28   | -41              | -29                  | -44.5                          | -45.5               | -43               | -36.5            | -34.5              | -45              | -49                 |
| $\delta^{18}O$   | -5.55   | -7.2             | -5.8                 | -7.69                          | -7.9                | -7.3              | -6.65            | -6.5               | -7.7             | -7.9                |
| Cl               | 39.1  | 26.6             | 22.2                 | 31.8                           | 39.3                | 29.1              | 25.3             | 24.3               | 33.6             | 21.2                |
| Na               | 26.6  | 26.6             | 24.9                 | 23.5                           | 28.5                | 21.6              | 23.9             | 24.7               | 29.8             | 17.6                |
| SiO <sub>2</sub> | 57.7  | 60.9             | 57                   | 58.7                           | 61.8                | 46.7              | 41.9             | 64.2               | 89.9             | 53.9                |
| Tracer           | Fall  |                  |                      | Winter                         |                     | Spring            |                  | Summer             |                  |                     |
|                  | <i>Tracer Concentrations in Groundwater</i>                           |                  |                      |                                |                     |                   |                  |                    |                  |                     |
| $\delta D$       | -47.2   |                  |                      | -46.2                          |                     | -44.4             |                  | -47                |                  |                     |
| $\delta^{18}O$   | -7.97   |                  |                      | -7.82                          |                     | -7.66             |                  | -7.97              |                  |                     |
| Cl               | 34.9  |                  |                      | 40.2                           |                     | 37.6              |                  | 35.6               |                  |                     |
| Na               | 30.5  |                  |                      | 31.4                           |                     | 30.4              |                  | 30.3               |                  |                     |
| SiO <sub>2</sub> | 96.5  |                  |                      | 84.4                           |                     | 78.7              |                  | 95.5               |                  |                     |

Here  $\delta$ , delta; D, deuterium;  $^{18}O$ , oxygen 18; Cl, chloride; Na, sodium; SiO<sub>2</sub>, silica;  $\delta D$  and  $\delta^{18}O$  given in per mille; Cl, Na, and SiO<sub>2</sub> concentrations given in micromoles per liter.

lysimeters in two soil pits: one in the steep north bank of the stream and the second in the less steep south bank (Figure 1b). The upper lysimeters were 0.10–0.15 m below land surface and the lower lysimeters were 0.46–0.51 m below land surface. The lysimeters were evacuated and sampled using a peristaltic pump each time storm flow samples were collected. The soil-water samples were assumed to reflect a combination of event water and pre-event water that had been pushed through the system by event water.

Stream stage near the outlet of the catchment was measured by a float mechanism and was recorded by a Campbell CR10 data logger. Discharge measurements [Buchanan and Somers, 1968, 1969] were made approximately every 6 weeks to develop log-log rating curves, with  $r^2$  values ranging from 0.97 to 0.99, from which instantaneous stream discharges were calculated [Kennedy, 1983, 1984]. Stream water samples were collected as grab samples from a point of maximum velocity in the stream near the streamflow gauging station. Storm flow samples were collected using an ISCO automatic sampler controlled by a stage-activated program on the CR10 data logger. The combi-

nation of fixed-interval and event sampling yielded a set of stream water samples that reflects a full range of sample types, including base flow through storm flow.

Although the main objective of studying the Bear Branch catchment was to monitor and assess the effects of acidic deposition, the data collected can be used to test the robustness of the three-component hydrograph separation technique. Storms for hydrograph separation were selected so that any additional precipitation that fell before or after the storm, included in the weekly throughfall sample, was minimal. This was achieved for 8 of the 10 storms (Table 1).

Aliquots of throughfall, soil-water, groundwater, and stream water samples for analysis of Cl<sup>-</sup>, Na<sup>+</sup>, and SiO<sub>2</sub> concentrations were filtered immediately after collection in the field through 0.1- $\mu$ m-pore-size cellulose nitrate filters, using positive pressure created by a peristaltic pump. Samples for analysis of Cl<sup>-</sup> concentration were stored at 4°C, and samples for analysis of Na<sup>+</sup> and SiO<sub>2</sub> concentrations were preserved with the addition of 200  $\mu$ L of Baker's InstrAnalyzed nitric acid. In the laboratory, samples were analyzed for Cl<sup>-</sup> concentration

using ion chromatography,  $\text{SiO}_2$  concentration using atomic-emission spectroscopy, and  $\text{Na}^+$  concentration using atomic-absorption spectrophotometry.

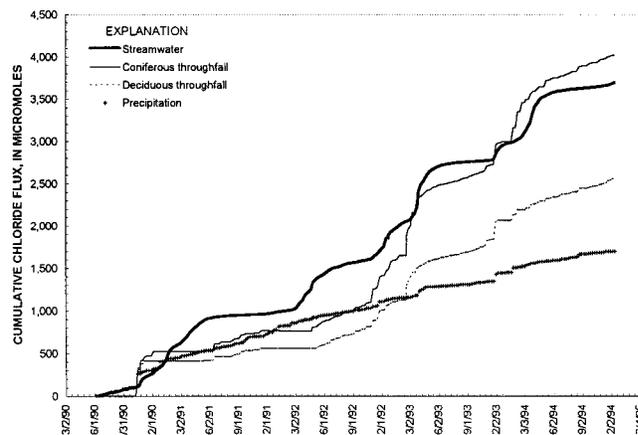
Aliquots of throughfall, soil-water, groundwater, and stream water samples also were collected for analysis of stable hydrogen- and oxygen-isotope activities. Sixty milliliters of unfiltered sample were decanted into a flint-glass bottle with a polyseal cap. Samples were analyzed for hydrogen-isotope activity using the method of Coplen *et al.* [1991]. Hydrogen-isotope results were expressed as  $\delta\text{D}$  in per mil (‰) relative to VSMOW (Vienna Standard Mean Ocean Water). The hydrogen-isotope method had a  $2\sigma$  precision of 2‰ (T. B. Coplen, U.S. Geological Survey, written communication, 1990). Samples were analyzed for oxygen-isotope activity using the method of Epstein and Mayeda [1953]. Oxygen-isotope results were expressed as  $\delta^{18}\text{O}$  in per mil relative to VSMOW and VPDB (Vienna Pee Dee belemnite). The oxygen-isotope method had a  $2\sigma$  precision of 0.2‰ (T. B. Coplen, written communication, 1990). Additional details of the sample-network design, and sample collection, processing, and analysis are described by Rice *et al.* [1996].

#### 4. Methods of Data Analysis

Hydrograph separations were performed by use of two methods: an iterative and an exact solution. With both approaches, separations were calculated for each of the seven pairs of tracers for the peak of the hydrograph for each storm.

Separé is a spreadsheet model that uses an iterative mass balance approach to calculate the percentages of three components that make up the composition of stream water at peak or other discharge [Sklash *et al.*, 1998]. Combinations of the contributions of the three components are multiplied by the values of a pair of tracers ( $\delta\text{D}$ ,  $\delta^{18}\text{O}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ , or  $\text{SiO}_2$ ) of each component. The process yields a set of calculated values of the tracers for the stream, which are compared to the observed values. The calculated values must match the observed values within 10 percentage points if throughfall is equal to 0, 10, 20, 30, 40, or 50%. If throughfall is equal to 5%, the soil-water contribution must be equal to 5–95%, in multiples of 10, and the calculated values must match the observed values within 5 percentage points. The user specifies the tolerance in the match between calculated and observed values. The tolerance takes into account a small amount of analytical error in the tracer concentrations. If the calculated and observed values agree within the tolerance allowed, an acceptable solution occurs. If no matches or too many matches are found, the tolerances are raised or lowered, respectively, and the process is repeated. Input requirements for Separé include the values and the tolerances of the two tracers for all three components and the observed values of the two tracers for the stream. Tolerances in Separé were set initially at  $\pm 2\%$  for  $\delta\text{D}$  and  $\delta^{18}\text{O}$ , and  $\pm 2 \mu\text{M}$  for  $\text{Cl}^-$ ,  $\text{Na}^+$ , and  $\text{SiO}_2$ , and were raised or lowered as necessary to obtain one match for the peak flow of each storm. For consistency and simplicity the tolerances of the two tracer pairs were kept equal, except for the  $\delta\text{D}$  and  $\delta^{18}\text{O}$  pair, where a larger tolerance for  $\delta\text{D}$  was allowed than for  $\delta^{18}\text{O}$ . Hydrograph separations at peak flow also were performed by directly solving (1)–(3) to obtain an exact solution.

The solution accepted by Separé was sometimes different than the exact solution. The difference is related to the process through which Separé partitions storm flow into the three end-members. Separé selects the value for the groundwater

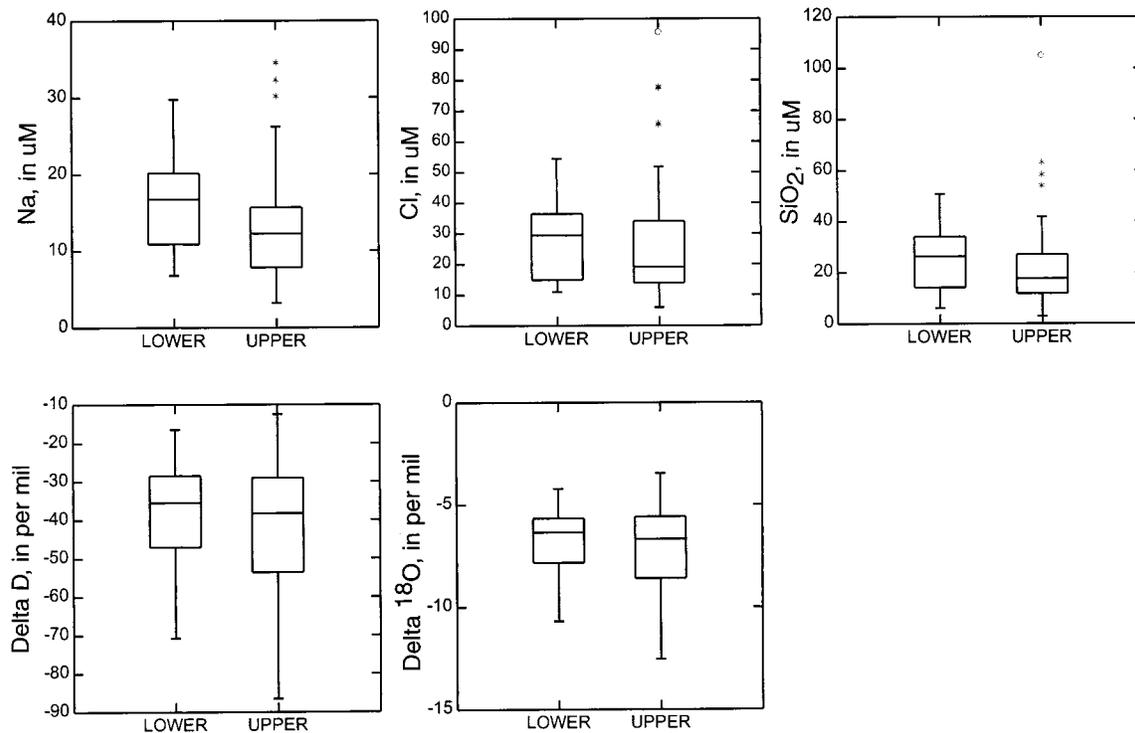


**Figure 2.** Cumulative chloride flux of stream water, coniferous throughfall, deciduous throughfall, and precipitation, June 5, 1990, through December 13, 1994.

component first, from 0 to 100, in multiples of 10. Next, Separé checks for the soil-water component (from 0 to 100, in multiples of 10; or from 5 to 95, in multiples of 10 when throughfall equals 5) and throughfall (from 0 to 50, in multiples of 10; or 5 if soil water is equal to 5–95, in multiples of 10). In some cases, particularly if the component mixing diagram was narrow and elongated, the selection of groundwater first, with restriction to multiples of 10, required the solution accepted by Separé to be different than the exact solution.

The tracer values of the throughfall component for each storm at peak flow were obtained from the weekly (or more frequent) composite sample of coniferous throughfall that included the storm (Table 1). Even though the majority of the catchment has deciduous tree canopy, coniferous throughfall was used as a source because the cumulative flux plot of  $\text{Cl}^-$  shows that coniferous throughfall influx most closely matches the streamwater efflux (Figure 2). No throughfall data were available for the March 6–10, 1992 storm, so the wet-only precipitation data for that week were used in the model and calculations.

The tracer values of the soil-water component for each storm at peak flow were obtained from the means of the samples collected after the storm from the upper and lower lysimeters (Table 1). The means of all soil-water data collected for each storm were used despite vertical and areal soil-water quality variability (Figure 3). The Kruskal-Wallis rank-sum test indicated that statistical differences between upper and lower soil-water chemistry ranged from 0.03 to 0.74. Only  $\text{Na}^+$  and  $\text{SiO}_2$  concentrations in the upper and lower soil waters could be considered significantly different at the 95% probability level. Upper and lower soil-water data were lumped for three reasons: (1) Differences in concentrations were not very significant ( $p > 0.10$ ) for all constituents except  $\text{Na}^+$  and  $\text{SiO}_2$ ; (2) no lower soil-water data were available for the October 23–24, 1990; June 18, 1991; August 19, 1991; or August 18–19, 1992, storms (the means of only the upper pans were used); and (3) physical evidence in soil pits did not indicate distinct differences in soil composition and texture between the upper and lower lysimeter locations, that is, no argillic soil horizons were present, despite the county soil-map designation of “Ultisol”; moreover, grain-size analysis of soil samples collected from a nearby catchment with the same bedrock type and



**Figure 3.** Box plots showing ion concentrations and isotopic compositions of samples collected from upper and lower lysimeters.

mapped soils indicated that the percentage of sand increased with depth and that the clay content at the depths of both lysimeters was 20% or less [Rice and Bricker, 1996].

To determine the tracer values of the groundwater component for each storm at peak flow, all stream samples were categorized as either base flow or storm flow on the basis of a visual determination from the annual hydrograph. Near-stream shallow groundwater in this system supplies base flow to the stream [Rice and Bricker, 1996]. An assumption not explicitly stated but usually implied for hydrograph separation is that the groundwater reservoir maintains a stable isotopic and chemical composition year-round. Relative to the other source end-members sampled in the catchment, groundwater maintains a stable isotopic (Figure 4a) and chemical composition (Figure 4b). The shallow groundwater that supplies base flow to the stream, however, does show seasonal isotopic (Figure 5a) and chemical variability (Figure 5b). Because of the seasonal variability, mean tracer values of base flow for the season in which the storm occurred were used for the groundwater component in the hydrograph separations (Table 1).

In order to assess the qualitative results of the hydrograph separations, the data were plotted on component mixing diagrams. Each pair of tracers of every streamflow sample for every storm was plotted; for each of the 70 plots, the peak of the hydrograph was identified and it was noted whether or not the peak fell within the confines of the triangle formed by the three end-members that had been sampled for that storm. If the peak flow value was constrained by the three end-members, the result was recorded as "good"; if the peak flow value did not fall within the triangle formed by the three end-members, the result was recorded as "bad"; and if the peak flow value fell on or just outside of one of the borders of the triangle, approximately within the analytical error for the tracers, the

result was recorded as "good/bad." In general, the sample collected at peak flow was a good indicator of the rest of the storm flow samples; that is, if the peak sample fell within the confines of the triangle, most of the rest of the storm flow samples also fell within the confines of the triangle. In addition, the pattern of the sequence of the storm flow samples was recorded on the mixing diagrams (Figure 6).

In cases where the stream composition at peak flow defined a point outside the triangle representing the end-members on a mixing diagram, no three-component hydrograph separation was possible. In such cases, there is an ambiguity regarding a separation into two hydrograph components. That is, the stream water may be considered a mixture of any two of the three end-members, or at least any two with compositions that bracket the stream water composition. The approach used in the exact solution was to choose the two components that defined the line on the mixing diagram to which the stream composition was closest. In all cases, this procedure identified either groundwater and soil water, or groundwater and throughfall, as the two components that mixed to form storm flow.

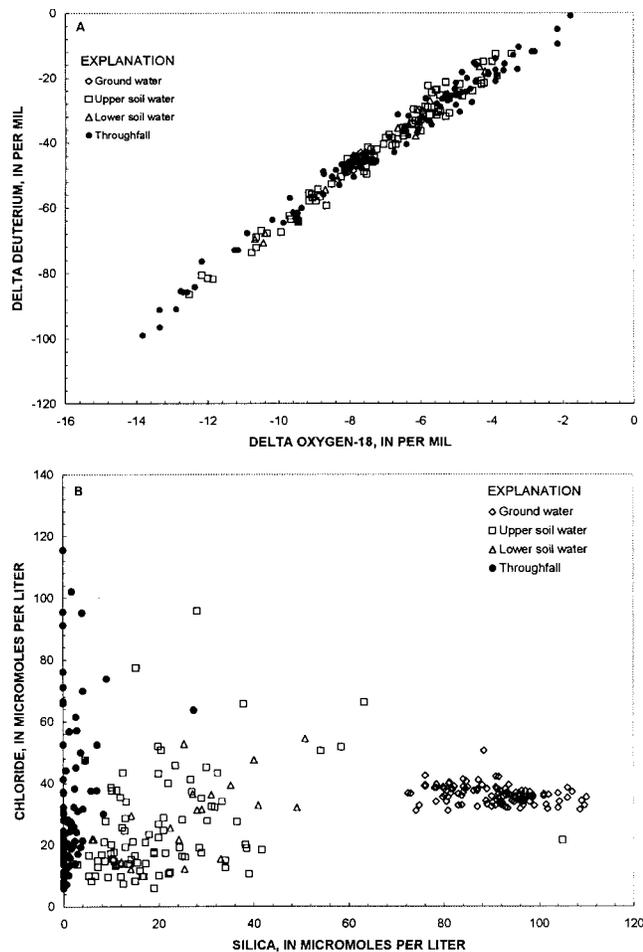
The effects of sampling errors of the three components were examined using a Monte Carlo approach. There are not enough data to estimate the sampling errors for our site. Previous studies indicate that 71 and 151 throughfall collectors are required to estimate Na<sup>+</sup> and Cl<sup>-</sup> concentrations, respectively, within 10% of the mean at the 95% confidence level [Kostelnik *et al.*, 1989; Puckett, 1991]. Arbitrary sampling errors of 5%, 10%, and 5% for groundwater, soil water, and throughfall, respectively, were assumed. These values were chosen merely to give an "indication" of the effects of errors on the separation results, and might be considered as "best-case scenario" sampling errors. For each storm the measured concentrations of

the three components were corrupted by “errors” chosen from a normal distribution with standard deviations given by the percentages above, and then the hydrograph components at peak flow were recalculated. The procedure was repeated 100 times for each storm, and the 25th and 75th percentiles (values in rank) were selected as an index of the variability in separation results.

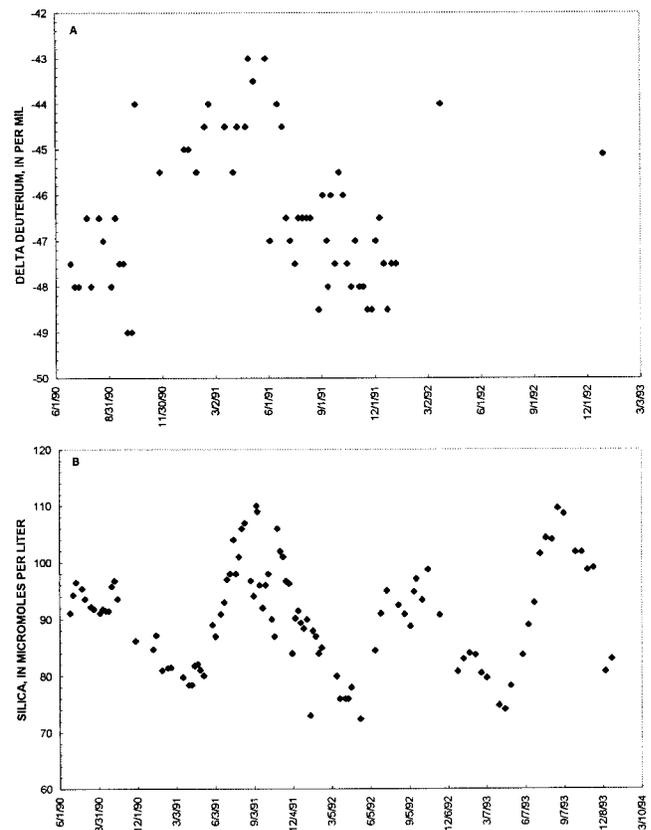
## 5. Results

Results of the hydrograph separations at peak flow using Separé were widely variable, with the range in the percentage of groundwater contribution determined from different tracer pairs for a single storm as narrow as 20 (e.g., 40–60% for August 18–19, 1992) to as wide as 40 (e.g., 50–90% for December 10–12, 1992) (Table 2). Results for the percentage of soil water and throughfall at peak flow were even more variable than for groundwater, with the range in the percentage of soil water as narrow as 20 (e.g., September 4, 1991) to as wide as 70 (April 21, 1992), and the range in the percentage of throughfall as narrow as 10 (e.g., March 6–10, 1992) to as wide as 50 (e.g., October 23–24, 1990).

Results of the hydrograph separations at peak flow using the



**Figure 4.** (a) Delta deuterium plotted against delta oxygen 18 in groundwater, upper and lower soil water, and coniferous throughfall. (b) Chloride concentrations plotted against silica concentrations in groundwater, upper and lower soil water, and coniferous throughfall.



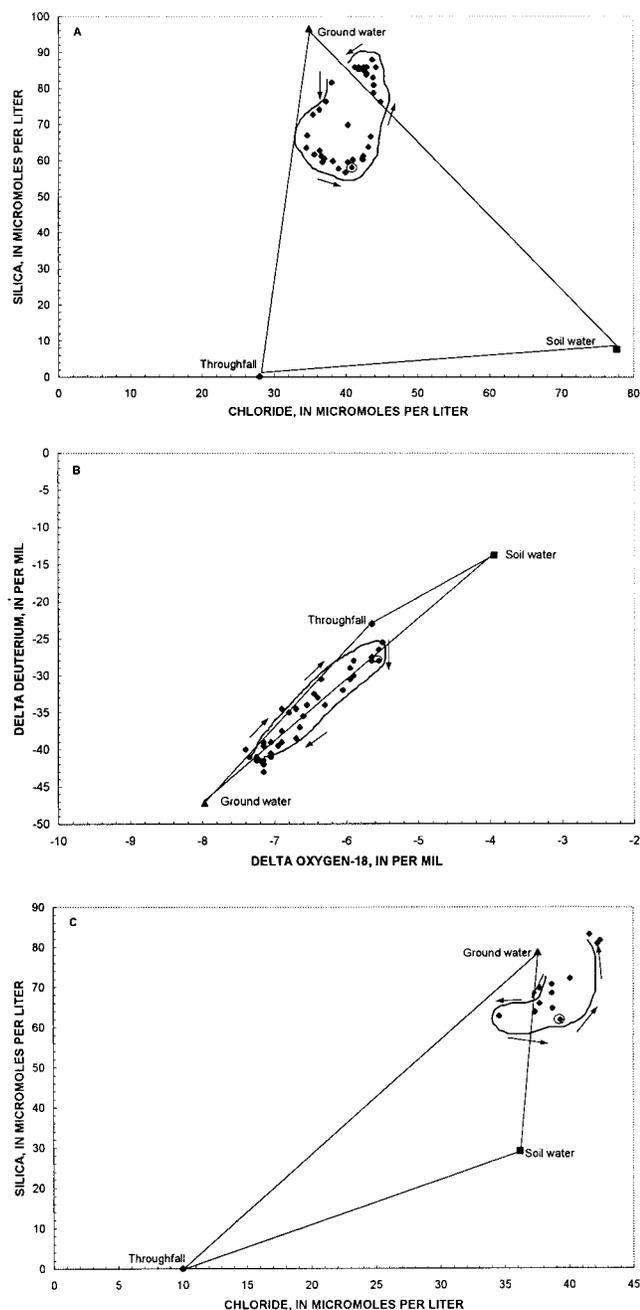
**Figure 5.** (a) Delta deuterium values in base flow, June 26, 1990, through December 29, 1992. (b) Silica concentrations in base flow, June 26, 1990, through December 29, 1993.

exact solution were also widely variable. The range in the percentage of groundwater contribution determined from different tracer pairs for a single storm were as narrow as 16 (August 19, 1991) to as wide as 67 (August 9–10, 1991); for soil water the intrastorm percentages ranged from 18 (August 19, 1991) to 91 (August 9–10, 1991); and for throughfall the intrastorm percentages ranged from 13 (August 19, 1991) to 57 (June 18, 1991) (Table 2).

The compilation of the tolerances (using Separé) of the tracers for each storm indicated that the tolerances of all of the tracers were reasonably low (less than 2.50) for only 3 of the 10 storms. For the other seven storms the tolerance of one or more sets of tracers had to be raised to 2.70 (and as high as 7.00) to force a solution to the mass balance equations (Table 2).

Results of the mixing diagram “good/bad” designations indicated that there were no storms with unanimously “good” designations; three storms had mixed “good” and “good/bad” designations; six storms had mixed “good” and (or) “good/bad” and “bad” designations; and one storm had unanimously “bad” designations. No pairs of tracers yielded unanimously “good,” “good/bad,” or “bad” designations (Table 2).

The exact solutions generally gave wider variability of percentages among the tracers for the separations than did Separé, because Separé accepts solutions defined by a tolerance parameter and calculates the solutions to the nearest 5% or 10% (Table 2). For the 24 “good” separations, Separé results and the exact solution differed by more than 10 percentage points in 2, 7, and 13 separations for the groundwater, soil-water, and throughfall components, respectively. For the 12



**Figure 6.** Example component mixing diagrams showing end-members and stream water samples. (Arrows indicate direction of evolution of stream water, and sample representing peak of the hydrograph is circled.) (a) “Good” mixing diagram for the October 23–24, 1990, storm. (b) “Good/bad” mixing diagram for the October 23–24, 1990, storm. (c) “Bad” mixing diagram for the March 6–10, 1992, storm.

“good/bad” separations, *Separé* results and the exact solution differed by more than 10 percentage points in 0, 4, and 3 separations for the groundwater, soil-water, and throughfall components, respectively. For the 34 “bad” separations, *Separé* results and the exact solution differed by more than 10 percentage points in 8, 12, and 5 separations for the groundwater, soil-water, and throughfall components, respectively.

Results of the Monte Carlo simulations for sampling error analysis were also highly variable (Table 2). The difference in

percentages between the 25th and 75th percentiles for all of the separations ranged from 2 to 87, 0 to 88, and 0 to 90 for groundwater, soil water, and throughfall, respectively. A 10-percentage-point or greater difference between the 25th and 75th percentiles occurred in 9 of the 10 storms (29% of the separations) for groundwater, all 10 storms (49% of the separations) for soil water, and all 10 storms (34% of the separations) for throughfall. The largest difference between the 25th and 75th percentiles for each component was 87 for the  $\delta D$  and  $\delta^{18}O$  tracer pair for groundwater, 88 for the  $\delta D$  and  $Cl^-$  tracer pair for soil water, and 90 for the  $\delta D$  and  $Cl^-$  tracer pair for throughfall. By tracer pair the difference between the two percentiles for any of the three components was 10 or greater for 25 separations using  $\delta D$  and  $\delta^{18}O$ , 18 separations using  $\delta D$  and  $Cl^-$ , 7 separations using  $\delta D$  and  $Na^+$ , 7 separations using  $\delta D$  and  $SiO_2$ , 6 separations using  $Cl^-$  and  $SiO_2$ , 6 separations using  $Cl^-$  and  $Na^+$ , and 9 separations using  $Na^+$  and  $SiO_2$ .

## 6. Discussion

In response to the first question posed in the introduction, Can three-component hydrograph separations be performed routinely in this catchment for all storms?, the answer is a qualified yes. The storms in the “good” category are those for which the exact solution assigned positive fractional flows to each of the three components. Nine of the 10 storms had at least one “good” separation (Table 2). But the answer to the unstated followup question, Are the results always meaningful?, is clearly no (Table 2). In some cases when using *Separé* the tolerances were raised higher than the normal analytical error in order to obtain a solution. In one case in using the exact solution, the groundwater component contributed more than 100% ( $\delta D$  and  $Cl^-$  for March 6–10, 1992; Table 2). In addition, in 27 of the separations (*Separé* and exact combined), soil-water contribution at the peak of the hydrograph was 0%. This is contrary to the accepted conceptual model of hillslope response during storm flow.

The sampling-error analysis using the Monte Carlo simulation of corrupted data indicated that none of the tracer pairs were immune to serious sampling error (greater than or equal to 10 percentage points) in the hydrograph separations. These results suggest that even with the best conditions for hydrograph separation, with only a 5% (groundwater or throughfall) or 10% (soil water) sampling error in one of the components, the hydrograph-separation results could be seriously in error.

The storms with the largest peak discharges and the wettest antecedent conditions (October 23–24, 1990; December 10–12, 1992; April 21, 1992; June 18, 1991; and August 18–19, 1992) produced the most favorable conditions for three- or two-component separations; that is, the most “good” and “good/bad” mixing diagrams (Tables 1 and 2; 30 “good” and “good/bad” versus 5 “bad”). These results are intuitively plausible because the assumptions for hydrograph separation are most likely to be met for large storms during wet conditions. In contrast, storms with smaller peak discharges and relatively dry antecedent conditions (September 4, 1991; September 18–19, 1991; March 6–10, 1992; August 9–10, 1991; and August 19, 1991) produced the most “bad” mixing diagrams (Tables 1 and 2; 29 “bad” versus 6 “good” and “good/bad”). Again, this is intuitively plausible because the components contributing to storm flow would be less well mixed as a result of low rainfall after a relatively long period of little or no rainfall.

The isotopic signatures of precipitation, throughfall, and

**Table 2.** Results of Hydrograph Separations at Peak Flow for 10 Storms in the Bear Branch Catchment, Catocтин Mountain, Maryland, October 1990 Through December 1992, Using a Variety of Tracers and Two Hydrograph-Separation Techniques

| Date and Season of Storm | Tracers                       | Percent Groundwater |       | Monte Carlo Groundwater "Errors" |      | Percent Soil Water |       | Monte Carlo Soil Water "Errors" |      | Percent Throughfall |       | Monte Carlo Throughfall "Errors" |      | Separé Tolerance of First/Second Tracer | Mixing Diagram, Good or Bad |
|--------------------------|-------------------------------|---------------------|-------|----------------------------------|------|--------------------|-------|---------------------------------|------|---------------------|-------|----------------------------------|------|---|-----------------------------|
|                          |                               | Separé              | Exact | 25th                             | 75th | Separé             | Exact | 25th                            | 75th | Separé              | Exact | 25th                             | 75th |   |                             |
| Oct. 23–24, 1990, fall   | $\delta D$ and $\delta^{18}O$ | 40                  | 40    | 33                               | 43   | 50                 | 60    | 54                              | 66   | 10                  | 0     | 0                                | 2    | 0.20/0.20                               | G/B                         |
|                          | $\delta D$ and Cl             | 30                  | 28    | 24                               | 31   | 20                 | 18    | 16                              | 20   | 50                  | 54    | 49                               | 60   | 1.50/1.50                               | G                           |
|                          | $\delta D$ and Na             | 30                  | 32    | 28                               | 36   | 30                 | 31    | 27                              | 35   | 40                  | 36    | 28                               | 44   | 1.00/1.00                               | G                           |
|                          | $\delta D$ and $SiO_2$        | 50                  | 56    | 55                               | 58   | 50                 | 44    | 42                              | 45   | 0                   | 0     | 0                                | 0    | 5.80/5.80                               | B                           |
|                          | Cl and $SiO_2$                | 60                  | 59    | 57                               | 60   | 10                 | 14    | 12                              | 16   | 30                  | 27    | 24                               | 30   | 2.00/2.00                               | G                           |
|                          | Cl and Na                     | 40                  | 49    | 45                               | 54   | 20                 | 16    | 14                              | 17   | 40                  | 35    | 29                               | 41   | 1.61/1.61                               | G                           |
| Sept. 4, 1991, fall      | Na and $SiO_2$                | 60                  | 59    | 58                               | 61   | 0                  | 6     | 1                               | 10   | 40                  | 35    | 28                               | 40   | 0.80/0.80                               | G                           |
|                          | $\delta D$ and $\delta^{18}O$ | 70                  | 68    | 59                               | 73   | 30                 | 5     | 0                               | 14   | 0                   | 27    | 6                                | 41   | 0.25/0.20                               | G                           |
|                          | $\delta D$ and Cl             | 50                  | 21    | 7                                | 28   | 40                 | 79    | 69                              | 88   | 10                  | 0     | 0                                | 0    | 3.70/3.70                               | B                           |
|                          | $\delta D$ and Na             | 70                  | 79    | 73                               | 83   | 30                 | 21    | 16                              | 27   | 0                   | 0     | 0                                | 0    | 1.80/1.80                               | B                           |
|                          | $\delta D$ and $SiO_2$        | 60                  | 63    | 58                               | 64   | 20                 | 0     | 0                               | 17   | 20                  | 37    | 24                               | 38   | 1.65/1.65                               | B                           |
|                          | Cl and $SiO_2$                | 60                  | 60    | 57                               | 62   | 40                 | 40    | 38                              | 43   | 0                   | 0     | 0                                | 0    | 4.20/4.20                               | B                           |
| Sept. 18–19, 1991, fall  | Cl and Na                     | 60                  | 79    | 73                               | 82   | 40                 | 21    | 17                              | 27   | 0                   | 0     | 0                                | 0    | 4.20/4.20                               | B                           |
|                          | Na and $SiO_2$                | 60                  | 60    | 57                               | 62   | 40                 | 40    | 0                               | 43   | 0                   | 0     | 0                                | 32   | 3.60/3.60                               | B                           |
|                          | $\delta D$ and $\delta^{18}O$ | 40                  | 44    | 42                               | 46   | 60                 | 28    | 0                               | 42   | 0                   | 29    | 8                                | 53   | 0.75/0.20                               | G                           |
|                          | $\delta D$ and Cl             | 50                  | 47    | 44                               | 50   | 0                  | 53    | 50                              | 56   | 50                  | 0     | 0                                | 0    | 1.65/1.65                               | B                           |
|                          | $\delta D$ and Na             | 60                  | 76    | 72                               | 79   | 10                 | 24    | 21                              | 28   | 30                  | 0     | 0                                | 0    | 5.20/5.20                               | B                           |
|                          | $\delta D$ and $SiO_2$        | 50                  | 53    | 51                               | 55   | 50                 | 47    | 45                              | 49   | 0                   | 0     | 0                                | 0    | 3.00/3.00                               | B                           |
| Dec. 10–12, 1992, winter | Cl and $SiO_2$                | 60                  | 53    | 52                               | 58   | 0                  | 47    | 0                               | 48   | 40                  | 0     | 0                                | 38   | 2.00/2.00                               | B                           |
|                          | Cl and Na                     | 60                  | 76    | 72                               | 79   | 40                 | 24    | 21                              | 28   | 0                   | 0     | 0                                | 0    | 3.80/3.80                               | B                           |
|                          | Na and $SiO_2$                | 60                  | 53    | 51                               | 55   | 20                 | 47    | 45                              | 49   | 20                  | 0     | 0                                | 0    | 4.65/4.65                               | B                           |
|                          | $\delta D$ and $\delta^{18}O$ | 90                  | 66    | 40                               | 70   | 10                 | 27    | 26                              | 41   | 0                   | 7     | 0                                | 19   | 0.30/0.20                               | G                           |
|                          | $\delta D$ and Cl             | 50                  | 44    | 36                               | 55   | 40                 | 42    | 31                              | 50   | 10                  | 14    | 14                               | 15   | 1.60/1.60                               | G                           |
|                          | $\delta D$ and Na             | 60                  | 63    | 60                               | 69   | 30                 | 29    | 20                              | 33   | 10                  | 8     | 7                                | 10   | 1.00/1.00                               | G                           |
| March 6–10, 1992, spring | $\delta D$ and $SiO_2$        | 60                  | 63    | 60                               | 68   | 35                 | 29    | 21                              | 33   | 5                   | 8     | 7                                | 11   | 2.00/2.00                               | G                           |
|                          | Cl and $SiO_2$                | 70                  | 70    | 68                               | 73   | 0                  | 0     | 0                               | 0    | 30                  | 30    | 27                               | 32   | 1.15/1.15                               | G/B                         |
|                          | Cl and Na                     | 70                  | 68    | 66                               | 72   | 0                  | 0     | 0                               | 0    | 30                  | 32    | 28                               | 34   | 1.15/1.15                               | G/B                         |
|                          | Na and $SiO_2$                | 60                  | 64    | 60                               | 70   | 40                 | 24    | 8                               | 33   | 0                   | 12    | 6                                | 20   | 0.50/0.50                               | G                           |
|                          | $\delta D$ and $\delta^{18}O$ | 80                  | 87    | 0                                | 87   | 10                 | 13    | 4                               | 34   | 10                  | 0     | 0                                | 57   | 0.25/0.15                               | G/B                         |
|                          | $\delta D$ and Cl             | 100                 | >100  | 47                               | 100  | 0                  | nfs   | 0                               | 50   | 0                   | nfs   | 0                                | 0    | 1.80/1.80                               | B                           |
| April 21, 1992, spring   | $\delta D$ and Na             | 90                  | 89    | 88                               | 96   | 10                 | 8     | 0                               | 6    | 0                   | 3     | 0                                | 8    | 0.56/0.56                               | G                           |
|                          | $\delta D$ and $SiO_2$        | 70                  | 74    | 73                               | 75   | 20                 | 12    | 6                               | 20   | 10                  | 14    | 4                                | 18   | 2.00/2.00                               | G                           |
|                          | Cl and $SiO_2$                | 70                  | 66    | 63                               | 72   | 30                 | 34    | 28                              | 36   | 0                   | 0     | 0                                | 0    | 2.50/2.50                               | B                           |
|                          | Cl and Na                     | 90                  | 87    | 82                               | 96   | 10                 | 13    | 4                               | 18   | 0                   | 0     | 0                                | 0    | 1.90/1.90                               | B                           |
|                          | Na and $SiO_2$                | 70                  | 66    | 62                               | 72   | 30                 | 34    | 28                              | 37   | 0                   | 0     | 0                                | 0    | 2.50/2.50                               | B                           |
|                          | $\delta D$ and $\delta^{18}O$ | 50                  | 41    | 0                                | 80   | 50                 | 59    | 18                              | 83   | 0                   | 0     | 0                                | 4    | 0.15/0.10                               | G/B                         |
| June 18, 1991, summer    | $\delta D$ and Cl             | 30                  | 33    | 31                               | 43   | 70                 | 67    | 54                              | 64   | 0                   | 0     | 0                                | 5    | 0.50/0.50                               | G/B                         |
|                          | $\delta D$ and Na             | 40                  | 43    | 41                               | 48   | 60                 | 57    | 48                              | 54   | 0                   | 0     | 0                                | 7    | 0.50/0.50                               | G/B                         |
|                          | $\delta D$ and $SiO_2$        | 50                  | 47    | 47                               | 50   | 45                 | 53    | 45                              | 52   | 5                   | 0     | 0                                | 7    | 1.50/1.50                               | G/B                         |
|                          | Cl and $SiO_2$                | 60                  | 55    | 53                               | 55   | 0                  | 19    | 13                              | 31   | 40                  | 26    | 14                               | 32   | 1.00/1.00                               | G                           |
|                          | Cl and Na                     | 50                  | 50    | 48                               | 53   | 30                 | 30    | 26                              | 35   | 20                  | 20    | 12                               | 24   | 0.50/0.50                               | G                           |
|                          | Na and $SiO_2$                | 60                  | 59    | 52                               | 60   | 0                  | 0     | 0                               | 42   | 40                  | 41    | 9                                | 41   | 0.56/0.56                               | G/B                         |
| Aug. 9–10, 1991, summer  | $\delta D$ and $\delta^{18}O$ | 50                  | 45    | 44                               | 50   | 10                 | 41    | 0                               | 42   | 40                  | 15    | 5                                | 45   | 0.20/0.10                               | G                           |
|                          | $\delta D$ and Cl             | 40                  | 42    | 34                               | 48   | 55                 | 56    | 50                              | 60   | 5                   | 2     | 0                                | 6    | 0.50/0.50                               | G                           |
|                          | $\delta D$ and Na             | 60                  | 73    | 69                               | 76   | 20                 | 0     | 0                               | 23   | 20                  | 27    | 0                                | 28   | 2.70/2.70                               | B                           |
|                          | $\delta D$ and $SiO_2$        | 40                  | 43    | 41                               | 44   | 10                 | 0     | 0                               | 0    | 50                  | 57    | 56                               | 58   | 3.50/3.50                               | B                           |
|                          | Cl and $SiO_2$                | 20                  | 14    | 8                                | 18   | 40                 | 49    | 45                              | 54   | 40                  | 37    | 35                               | 38   | 1.80/1.80                               | G                           |
|                          | Cl and Na                     | 60                  | 70    | 66                               | 74   | 40                 | 30    | 26                              | 34   | 0                   | 0     | 0                                | 0    | 3.00/3.00                               | B                           |
| Aug. 19, 1991, summer    | Na and $SiO_2$                | 50                  | 43    | 41                               | 44   | 0                  | 0     | 0                               | 0    | 50                  | 57    | 56                               | 59   | 7.00/7.00                               | B                           |
|                          | $\delta D$ and $\delta^{18}O$ | 60                  | 62    | 55                               | 64   | 0                  | 0     | 0                               | 40   | 40                  | 38    | 0                                | 41   | 1.11/0.20                               | B                           |
|                          | $\delta D$ and Cl             | 40                  | 9     | 5                                | 19   | 60                 | 91    | 0                               | 88   | 0                   | 0     | 0                                | 90   | 4.48/4.48                               | B                           |
|                          | $\delta D$ and Na             | 60                  | 76    | 72                               | 78   | 40                 | 24    | 21                              | 28   | 0                   | 0     | 0                                | 0    | 3.70/3.70                               | B                           |
|                          | $\delta D$ and $SiO_2$        | 60                  | 62    | 59                               | 64   | 40                 | 38    | 36                              | 41   | 0                   | 0     | 0                                | 0    | 1.50/1.50                               | B                           |
|                          | Cl and $SiO_2$                | 60                  | 62    | 59                               | 66   | 40                 | 38    | 30                              | 41   | 0                   | 0     | 0                                | 0    | 6.35/6.35                               | B                           |
| Aug. 18–19, 1992, summer | Cl and Na                     | 50                  | 76    | 72                               | 79   | 50                 | 24    | 8                               | 28   | 0                   | 0     | 0                                | 0    | 6.00/6.00                               | B                           |
|                          | Na and $SiO_2$                | 70                  | 66    | 62                               | 67   | 0                  | 0     | 0                               | 0    | 30                  | 34    | 31                               | 36   | 3.50/3.50                               | B                           |
|                          | $\delta D$ and $\delta^{18}O$ | 80                  | 82    | 69                               | 89   | 20                 | 18    | 0                               | 24   | 0                   | 0     | 0                                | 11   | 0.25/0.10                               | B                           |
|                          | $\delta D$ and Cl             | 80                  | 83    | 71                               | 92   | 0                  | 4     | 3                               | 6    | 20                  | 13    | 4                                | 24   | 0.75/0.75                               | G                           |
|                          | $\delta D$ and Na             | 100                 | 98    | 94                               | 100  | 0                  | 2     | 0                               | 3    | 0                   | 0     | 0                                | 2    | 2.00/2.00                               | B                           |
|                          | $\delta D$ and $SiO_2$        | 90                  | 93    | 90                               | 96   | 10                 | 7     | 0                               | 8    | 0                   | 0     | 0                                | 5    | 3.00/3.00                               | B                           |
| Aug. 18–19, 1992, summer | Cl and $SiO_2$                | 90                  | 93    | 89                               | 96   | 10                 | 7     | 4                               | 11   | 0                   | 0     | 0                                | 0    | 3.00/3.00                               | B                           |
|                          | Cl and Na                     | 100                 | 98    | 94                               | 100  | 0                  | 2     | 0                               | 6    | 0                   | 0     | 0                                | 0    | 2.05/2.05                               | B                           |
|                          | Na and $SiO_2$                | 90                  | 94    | 90                               | 97   | 10                 | 0     | 0                               | 0    | 0                   | 6     | 3                                | 10   | 3.20/3.20                               | B                           |
|                          | $\delta D$ and $\delta^{18}O$ | 40                  | 29    | 19                               | 34   | 10                 | 16    | 4                               | 28   | 50                  | 55    | 49                               | 59   | 0.20/0.15                               | G                           |
|                          | $\delta D$ and Cl             | 50                  | 49    | 45                               | 51   | 10                 | 7     | 0                               | 18   | 40                  | 44    | 36                               | 47   | 0.50/0.50                               | G                           |

**Table 2.** (continued)

| Date and Season of Storm | Tracers                | Percent Groundwater |       | Monte Carlo Groundwater "Errors" |      | Percent Soil Water |       | Monte Carlo Soil Water "Errors" |      | Percent Throughfall |       | Monte Carlo Throughfall "Errors" |      | Separé Tolerance of First/Second Tracer | Mixing Diagram, Good or Bad |
|--------------------------|------------------------|---------------------|-------|----------------------------------|------|--------------------|-------|---------------------------------|------|---------------------|-------|----------------------------------|------|---|-----------------------------|
|                          |                        | Separé              | Exact | 25th                             | 75th | Separé             | Exact | 25th                            | 75th | Separé              | Exact | 25th                             | 75th |   |                             |
| Aug. 18–19, 1992, summer | $\delta D$ and Na      | 60                  | 57    | 52                               | 58   | 0                  | 4     | 0                               | 14   | 40                  | 39    | 32                               | 41   | 1.00/1.00                               | G                           |
|                          | $\delta D$ and $SiO_2$ | 50                  | 55    | 51                               | 57   | 20                 | 5     | 0                               | 15   | 30                  | 40    | 33                               | 42   | 3.00/3.00                               | G                           |
|                          | Cl and $SiO_2$         | 50                  | 45    | 42                               | 47   | 30                 | 55    | 53                              | 57   | 20                  | 0     | 0                                | 0    | 1.50/1.50                               | G/B                         |
|                          | Cl and Na              | 50                  | 48    | 46                               | 50   | 30                 | 52    | 50                              | 54   | 20                  | 0     | 0                                | 0    | 1.10/1.10                               | G/B                         |
|                          | Na and $SiO_2$         | 50                  | 56    | 54                               | 57   | 30                 | 0     | 0                               | 0    | 20                  | 44    | 42                               | 46   | 1.00/1.00                               | G/B                         |

Here,  $\delta$ , delta; D, deuterium;  $^{18}O$ , oxygen 18; Cl, chloride; Na, sodium;  $SiO_2$ , silica; nfs, no feasible solution; 25th, 25th percentile; 75th, 75th percentile; G, good; B, bad; G/B, good/bad. Separé refers to results obtained using an iterative solution. "Exact" refers to results obtained using an exact solution; exact solution results were rounded to the nearest whole number, with the result that the three components for some tracer pairs do not total to exactly 100.

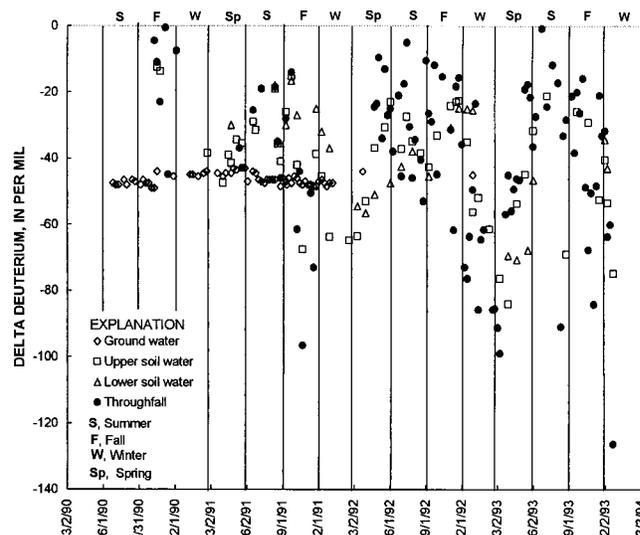
upper and lower soil waters show a seasonal pattern (Figure 7). Because cold temperatures increase isotopic fractionation of precipitation, the maximum amount of isotopic fractionation occurs during the winter, and the minimum amount occurs during the summer. The soil-water signatures are more subdued than those of the input signatures. In addition, the soil-water signatures slightly lag the input signatures, with lower soil water lagging more than upper soil water. This lagging with time and damping with depth of the soil-water isotopic signatures causes three-component hydrograph separations to be more difficult to do "cleanly" than if the soil water had a more distinctly different composition from that of groundwater. The "cleanest" three-component hydrograph separations should be able to be made during seasons when soil-water and groundwater compositions are the most dissimilar. There were no seasons in which there was consistently good isotopic separation between upper soil water and throughfall (Figure 7). In three of the seasons, however, there was enough difference in composition of the two end-members that a clean separation could be made. This observation is borne out by hydrograph-separation results where a winter storm (December 10–12, 1992), a spring storm (April 21, 1992), and a summer storm (August 18–19, 1992) had only "good" or "good/bad" mixing-diagram designations for tracer pairs that included  $\delta D$  (Table 2). These three storms were also members of the "wet" group, where moist antecedent conditions and high rainfall during the storm helped make conditions favorable for three-component hydrograph separation, as discussed previously.

The answer to the second question, Are consistent quantitative results obtained using different pairs of chemical and isotopic tracers?, is no (Table 2). Of the 70 hydrograph separations performed with Separé, only 28 of the pairs of tracers gave the same results (within 10 percentage points) for each component as at least one other pair of tracers for the same storm, and for separations solved with the exact solution, only 39 of the pairs of tracers gave the same results (within 5 percentage points) for each component as at least one other pair of tracers for the same storm. These results imply that a three-component hydrograph-separation from one storm in a catchment, using one set of tracers, could be highly suspect.

The third question posed in the introduction, Are consistent patterns in the results observed?, can be answered by examining the mixing diagrams in conjunction with the separation results. In general, consistent patterns in the hydrograph-separation results were observed. Groundwater contributed at

least 50% to the peak of the hydrograph in 65% of the hydrograph separations that had "good" mixing diagrams. Total subsurface water (groundwater plus soil water) contributed from 45% 100% to peak flow in all cases. This result is consistent with the range in subsurface fractions identified in forested catchments worldwide [Buttle, 1994].

The fourth question posed in the introduction, Can a reasonable conceptual model be developed for the patterns observed?, also can be answered by examining the mixing diagrams. Of the 24 "good" mixing diagrams, all but 3 showed the pattern of storm flow contributions first deriving from groundwater, then throughfall, then soil water, and back to groundwater as the hydrograph receded. A conceptual model to explain the observed pattern is this: (1) Streamflow is provided by groundwater at the beginning of the storm; (2) as precipitation continues, direct interception of throughfall on the stream channel begins to change the stream water composition; (3) as the storm continues, more water infiltrates the ground surface and percolates downward through the soil column and soil water begins to contribute to storm flow; and finally, (4) as precipitation tapers off, throughfall and soil-water contribu-



**Figure 7.** Delta deuterium values of groundwater, upper and lower soil water, and coniferous throughfall, June 26, 1990, through December 21, 1993.

tions cease and stream flow once again is provided by groundwater. Of the 24 "good" mixing diagrams, the three exceptions that did not follow this pattern were from one storm (June 18, 1991). In this storm the sequence was groundwater, soil water, then throughfall, and back to groundwater. We do not have an explanation for this pattern. It is possible, however, that the additional throughfall included in the weekly sample contributed to sampling error so that the source components were not properly identified for the storm (Table 1). Although the "good/bad" and "bad" mixing diagrams indicated problems with three-component separations, the pattern identified in the "good" mixing diagrams (groundwater, throughfall, soil water, groundwater) usually held for the "good/bad" and "bad" mixing diagrams as well (e.g., Figure 6).

## 7. Summary

After more than two decades of performing hydrograph separations in small, forested, temperate-zone catchments, what has been learned? Subsurface water (groundwater, or groundwater and soil water) contributes most of the water to storm flow, over and over, in catchment after catchment [Buttle, 1994]. More than two decades ago, researchers performing hydrograph separations [e.g., Fritz *et al.*, 1974; Mook *et al.*, 1974; Sklash *et al.*, 1976] came to this same conclusion. Even if the assumptions of hydrograph separation have not been met, and (or) end-member compositions have not been properly identified, the result of the hydrograph separation is the same: Subsurface water in upland forested catchments dominates storm flow. Many researchers continue to focus on hydrograph separation in new catchments with new chemical and (or) isotopic data. This study, however, demonstrates that flow components cannot be unambiguously identified using chemical and (or) isotopic measurements alone. Studies such as those by Jenkins *et al.* [1994], Elsenbeer and Lack [1996], and Anderson *et al.* [1997] have coupled hydrochemical and hydrometric measurements. For continued advances, hydrochemical and hydrometric measurements need to be coupled in order to perform meaningful hydrograph separations.

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