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The role of event water, a rapid shallow flow component, and catchment size in summer stormflow

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Abstract

Seven nested headwater catchments (8 to 161 ha) were monitored during five summer rain events to evaluate storm runoff components and the effect of catchment size on water sources. Two-component isotopic hydrograph separation showed that event-water contributions near the time of peakflow ranged from 49% to 62% in the 7 catchments during the highest intensity event. The proportion of event water in stormflow was greater than could be accounted for by direct precipitation onto saturated areas. DOC concentrations in stormflow were strongly correlated with stream ^{18}O composition. Bivariate mixing diagrams indicated that the large event water contributions were likely derived from flow through the soil O-horizon. Results from two-tracer, three-component hydrograph separations showed that the throughfall and O-horizon soil-water components together could account for the estimated contributions of event water to stormflow. End-member mixing analysis confirmed these results. Estimated event-water contributions were inversely related to catchment size, but the relation was significant for only the event with greatest rainfall intensity. Our results suggest that perched, shallow subsurface flow provides a substantial contribution to summer stormflow in these small catchments, but the relative contribution of this component decreases with catchment size.

Keywords: Stormflow; Two-tracer three-component hydrograph; Two-component isotopic separation; End-member mixing analysis

1. Introduction

Recent research in hillslope hydrology has determined the physical mechanisms responsible for stormflow generation and their effect on the chemistry of drainage waters (Bishop et al., 1990; Mulholland et al., 1990; Jenkins et al., 1994). Generally, flow pathways that dominate during storm or snowmelt events determine the resulting surface water chemistry during and after the event (Bonell, 1993). The relative importance of these flowpaths may vary both spatially and temporally, thereby preventing a simple conceptualization of the hydrochemical response (Genereux et al., 1993; Elsenbeer et al., 1994). Many of the physical mechanisms that rapidly deliver water to the stream channel may occur in the same catchment depending on antecedent moisture conditions (Elsenbeer et al., 1994), rainfall intensity (McDonnell, 1990), soil depth variability (Ross et al., 1994), and/or underlying bedrock topography (Brammer and McDonnell, 1996).

Combined physical and tracer-based approaches

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can characterize the source, residence time, and flowpaths of water in small catchments (McDonnell, 1990; Waddington et al., 1993; Bonell et al., 1998). Different flow pathways often exhibit similar isotopic, hydrologic, or hydrochemical responses, indicating that a combination of hydrometric, isotopic, and hydrochemical data are necessary to obtain unequivocal results (Bonell, 1993; Buttle, 1994). Hydrometric data define the timing of the hydrological response, and isotopic and hydrochemical data can determine the relative contributions of water stored in different locations to the overall catchment response (Bonell et al., 1998). Isotopes can provide data on hydrologic sources, whereas hydrochemical data can elucidate water flowpaths (Wels et al., 1991). Isotopic and hydrochemical data together with hydrometric data can provide a perceptual model of the catchment response (Ambroise et al., 1996).

Most studies in temperate upland forested catchments have determined streamflow generation mechanisms that occur when antecedent moisture conditions are high and moisture deficits are low; for example during spring snowmelt (Hooper and Shoemaker, 1986; Wels et al., 1990; Waddington et al., 1993), or in high rainfall areas (e.g. Pearce et al., 1986; McDonnell, 1990). These studies have generally shown that pre-event water (water that resides in the catchment prior to the onset of rainfall or snowmelt) contributes about 70%–96% of streamflow at the hydrograph peak. One study of summer stormflow generation during dry conditions concluded that pre-event water may still dominate the storm hydrograph due to the rapid mobilization of near-stream groundwater (Sklash and Farvolden, 1979). Other studies have shown that mobilized soil water in addition to event water are important contributors to stormflow during dry periods, despite high soil moisture deficits (Fritz et al., 1976; Pionke et al., 1993; Bazemore et al., 1994).

The physical mechanisms by which soil water and groundwater reach the stream during dry conditions in temperate upland forested catchments remain poorly understood. DeWalle and Pionke (1994) described the contribution from shallow subsurface flow when rainfall magnitude and intensity are great enough to cause the water table to rise close to the soil surface. The importance of saturated flow from the shallow subsurface is often linked to the typical decline in hydraulic conductivity with increasing soil depth. This process, known as transmissivity feedback, was studied and described in detail by Bishop et al. (1990) during relatively dry antecedent conditions, when storm runoff originated from within the upper four decimeters of soil in an area 50 m wide adjacent to the stream channel.

The development of perched saturation in shallow soil horizons on steep hillslopes is also an important subsurface flowpath that contributes to rapid stormflow (Chappell et al., 1990; Jenkins et al., 1994). This process has been described by McDonnell et al. (1991) as pseudo-Hortonian overland flow, whereby large differences in saturated hydraulic conductivity at the organic–mineral soil boundary create lateral flow in the near-surface horizon. Lateral flow in the near-surface soil horizons explained the hydrologic response in the riparian zone of a Welsh catchment, an observation that was corroborated by the chemical similarity of near-surface soil water and riparian zone water (Chappell et al., 1990). The hydrophobic nature of organic matter in the soil O-horizon may also contribute to increased lateral flow.

Variability in the concentration of dissolved organic carbon (DOC) in streamwater may be an effective indicator of flowpaths during storm runoff, and DOC concentrations typically vary with stream discharge (McDowell and Fisher, 1976; Moore, 1989; Fiebig et al., 1990). Fiebig et al. (1990) showed that soil water DOC was efficiently immobilized in the streambed during baseflow, but increases of DOC concentrations in streamwater during higher flow conditions could be explained by the flushing of areas along preferential flowpaths further from the stream channel in the riparian zone that did not contribute to the hydrograph during low-flow conditions. By modeling hydrologic controls on DOC, Hornberger et al. (1994) suggested that flushing from soil sources was the most important mechanism affecting DOC concentrations. Streamwater DOC concentrations may, therefore, be an indicator of contributions from a rapid event-based shallow subsurface flowpath.

Little is known about the effect of catchment size on the relative source and flowpath contributions to summer stormflow. Pearce (1990) found that isotopically derived event-water contributions to stormflow increased with increasing drainage area in four nested

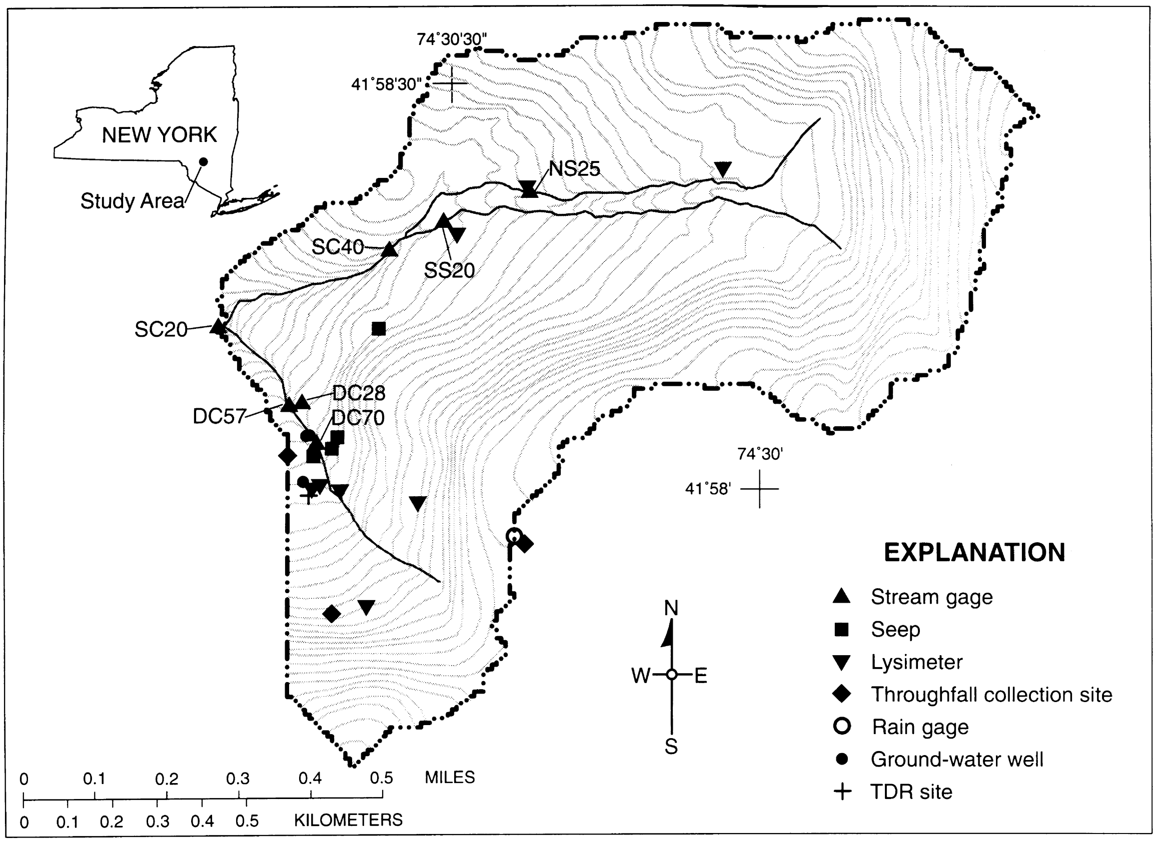

Fig. 1. Map of Shelter Creek catchment, Catskill Mountains, New York. Inset of location within New York state. Also mapped are locations of weir or flume sites, lysimeter sites, throughfall collection sites, throughfall and rain gages, groundwater well site, TDR site and seeps sampled in this study.

catchments (ranging from a < 500 m^2 hillslope zero-order basin to a 2.8 km^2 third-order stream). Larger proportions of valley floor saturated areas accounted for larger volumes of saturated overland flow consistent with greater event water flow.

The study described in this paper is part of a larger multi-disciplinary study of the effects of forest harvesting practices on the biogeochemistry of nitrogen in the Catskill Mountains of New York (Burns et al., 1997). Stream nitrate concentrations in the Catskills have increased in recent years in association with decreased pH and increased aluminium concentrations (Murdoch and Stoddard, 1992; Murdoch and Stoddard, 1993). The flow-related changes in stream nitrate concentrations observed in the Catskills (Murdoch and Stoddard, 1992) have suggested the need for additional studies that describe changes in hydrologic flowpaths during rain events.

This paper describes results from a series of summer rainstorms during July 1995 at nested headwater catchments in the Catskill Mountains of New York that range from 8 to 161 ha. Multiple isotopic and chemical hydrograph separation techniques were utilized together with hydrometric data to determine: (1) the contribution of event water to summer stormflow, (2) the role of a shallow subsurface water flow component in summer stormflow generation, and (3) the influence of catchment size on storm runoff response, event water contributions, and the relative contribution from shallow subsurface flow.

2. Study area

Shelter Creek (SC20) is a 161-ha forested catchment that drains into the West Branch of the Neversink River in the Catskill Mountains of New York State (Fig. 1). Elevation ranges from 695 to 985 m in the catchment. Mean annual temperature is 4.3°C at the Slide Mountain weather station, 10 km from the study area. Mean annual precipitation is 1500 mm, of which about 20% falls as snow (Stoddard and Murdoch, 1991). Although precipitation amounts are uniformly distributed throughout the year, summer conditions in the catchment are drier than are those of other seasons. Underlying bedrock is composed of flat-lying sedimentary units of Devonian age that consist of 60% sandstone and conglomerate and 40% siltstone and mudstone (Ethridge, 1977). Bedrock is generally overlain by 0.25–1.5 m of glacial till that can range from clay-size particles to boulders. Soils are Inceptisols in the Arnot–Oquaga–Lackawanna association and are described as excessively to moderately well-drained (Tornes, 1979). Dominant tree species in this northern hardwood forest include American beech (*Fagus granidifolia*), sugar maple (*Acer saccharum*), and yellow birch (*Betula alleghaniensis*). Stands of hemlock (*Tsuga canadiensis*) grow on poorly drained soils.

Seven nested subcatchments ranging from 8 to 161 ha were monitored at weirs and flumes. Subcatchments DC28, DC70, DC57, NS25, SS20, and SC40 are 8, 11, 24, 33, 51, and 109 ha in drainage area, respectively. Dry and Shelter Creeks converge just upstream of weir SC20 (Fig. 1). The Dry Creek subcatchments and the upper reaches of the Shelter Creek subcatchments are characterized by deeply incised stream channels. Streams in the Shelter Creek catchment are also characterized by the presence of groundwater seeps, or springs, that emerge from the hillslope as pipeflow and provide an important component of baseflow (Burns et al., 1998).

Streamflow in Dry Creek during the summer originates about 15 m upslope of the weir at DC70, where a perennial seep maintains baseflow at the weir. DC57 is 100 m downstream from DC70, and between these sites are two small seep channels that drain into the main stream channel. The DC28 weir is fed by a seep 100 m upslope from the weir that maintains soil saturation in the adjacent low-relief area of the seep channel. SS20 is also in the lower part of a region of low relief where the divide between the two parallel creeks is indistinct. The NS25 flume is fed by North Shelter Creek and is slightly higher in the catchment where streams are more deeply incised.

3. Method

3.1. Sampling and laboratory methods

The seven catchments were monitored and sampled with automated samplers during five rain events in July 1995. Six source components of stormflow were sampled – throughfall, seepwater, near-stream groundwater, and soil water from the O, B, and C horizons.

Flow in the Shelter Creek catchments was monitored at three weirs and four flumes, each with stage-activated automated water samplers. Stage was measured by a pressure transducer and recorded on a datalogger every 15 min. Baseflow samples and seepwater samples from each catchment were collected biweekly.

Precipitation and throughfall amounts were measured in weighing-bucket gages. Throughfall was sampled weekly at three sites for chemical analysis; each site consisted of ten funnel collectors. Throughfall was also sampled in 6 mm increments for ^{18}O analysis during each event by a sequential sampler.

Soil water was sampled at ten nests of zero-tension soil lysimeters at three soil depths (O, B and C horizons). Samples were pumped from a 4-L capacity vessel that was set underground and gravity fed by 3 collection disks of 150 mm diameter, installed under the soil horizon that was sampled. The volume of water collected from each zero-tension pan lysimeter was recorded, and was considered indicative of the relative amount of flow through the soil horizon. Lysimeter samples were collected three times during the study period.

Soil water was recorded every 2 h at one site by 15 time-domain-reflectometry (TDR) rod pairs at 5 depths. TDR rod pairs were located at the base of the O-horizon soil at a depth of 58 mm; in the B-horizon at depths of 280, 330, 330 and 480 mm; and in the C-horizon at a depth of 685 mm. Rod pairs were not calibrated before use; therefore, water-content data reported here are relative, rather than absolute values.

Groundwater level was continuously monitored with a 10-turn potentiometer at a 15 cm diameter well in an upslope position in the Dry Creek catchment (Fig. 1). Near-stream groundwater samples were collected biweekly from two observation wells 1 and 2 m from Dry Creek.

All samples were refrigerated until analyzed. Major anions and cations, as well as DOC, were analyzed by the USGS laboratory in Troy, NY. Samples for Cl^- and SO_4^{2-} analysis were passed through 0.4 μm filters and analyzed by ion chromatrography, and reported to within 10% error and coefficient of variation (cv) of 15%. Samples for DOC analysis were passed through a 0.7 μm GF/F glass fiber filter prior to analysis by infrared detection according to the analytical method described by Lawrence et al. (1995) and reported to within 15% error and cv of 15%. Samples were analyzed for $\delta^{18}O$ by the USGS laboratory in Menlo Park, CA and values are reported relative to V-SMOW with a 1-standard deviation precision of 0.05‰.

Catchment areas were measured by walking the topographic boundaries with a global positioning system (GPS) unit. Areas within mapped boundaries were calculated through a polygon-area feature by geographic information system software. Stream channel areas were estimated by walking selected streams with a GPS unit to determine stream length, whereas the lengths of other streams were estimated from maps. Errors in these estimates could result from intermittent flow in rivulets that were not observed at baseflow. Some rivulets were observed during events, but were not considered to be of significant areal extent relative to the total stream channel area.

3.2. Hydrograph separation techniques

The hydrographs separation techniques applied in this study were: (1) quickflow (Hewlett and Hibbert, 1967), (2) two-component isotopic separation (Pinder and Jones, 1969; Sklash and Farvolden, 1979), (3) two-tracer three-component separation (Ogunkoya and Jenkins, 1993), and (4) end-member mixing analysis (Christophersen and Hooper, 1992).

1. *Quickflow*. The hydrograph of each subcatchment was separated into quickflow and delayed flow, as described by Hewlett and Hibbert (1967). This method was used to consistently compare and describe stormflow among catchments for the different events. A separation line was projected from the initial rise of the hydrograph at a slope of 0.0055 1 s^{-1} ha^{-1} h^{-1}(0.05 ft^3 sq mi^{-1} h^{-1}) until it intersected the receding limb of the hydrograph.
2. *Two-component isotopic separation*. The two-component isotopic separation (Pinder and Jones, 1969; Sklash and Farvolden, 1979) is a mass-balance approach that separates stormflow into pre-event water (stored in the catchment prior to the event) and event water on the basis of the stable isotope ratios of each component:

$$Q_tC_t = Q_pC_p + Q_eC_e \tag{1}$$

where Q is discharge, C is $\delta\,^{18}$O composition, and the subscripts t, p and e represent the total streamflow, pre-event, and event components, respectively. The relative contributions of event and pre-event water to stormflow were calculated for each streamwater sample collected. The event-water component was calculated as the incremental weighted mean of the isotopic composition of throughfall (McDonnell et al., 1990) to account for temporal variability. The isotopic composition of baseflow represented the pre-event component. The uncertainty associated with the computed mixing fractions was evaluated using the technique described by Genereux (1996):

$$W_{fp} = \sqrt{\left[\frac{C_e - C_s}{(C_e - C_p)^2} W_{Cp}\right]^2 + \left[\frac{C_S - C_p}{(C_e - C_p)^2} W_{Ce}\right]^2 + \left[\frac{1}{(C_p - C_e)} W_{Cp}\right]^2} \tag{2}$$

where W is uncertainty, C is the tracer concentration, f is the mixing fraction, and the subscripts p, e, and s refer to pre-event, event and stream water components.

Table 1
Throughfall characteristics for July 1995 events and pre-storm baseflow at SC20

	7-Jul	17-Jul	23-Jul	26-Jul	27-Jul
Magnitude (mm)	9.9	34.0	8.5	32.7	13.9
Duration (h)	5.0	12.3	5.5	9.8	2.8
Avg intensity (15 min)	0.8	1.3	1.2	3.6	2.0
Max intensity (15 min)	1.5	7.0	7.2	10.9	6.2
Baseflow at SC20 prior to event (mm/hr)	0.023	0.012	0.011	0.012	0.018

3. *Two-tracer three-component separation*. The three-component hydrograph separation with two tracers was used as described by Ogunkoya and Jenkins (1993):

$$Q_tC_t = Q_1C_1 + Q_2C_2 + \ldots + Q_mC_m \quad (3)$$

where the subscripts 1,2, …, m are the assumed components of total storm runoff, and n tracers are needed to partition the hydrograph into (n + 1) components. The above equation can be written in matrix form using the notation of Christophersen and Hooper (1992):

$$\mathbf{x_i} = \mathbf{l_i}\mathbf{B} \quad (4)$$

where $\mathbf{x_i}$ is any single observation of streamwater which is a $1 \times p$ vector of p solutes. The matrix $\mathbf{B}$ describes the solute concentrations of end members and has dimensions $k \times p$, i.e., k end members and p solutes. The vector $\mathbf{l_i}$ is the $1 \times k$ vector of the proportion of those end members contributing to total flow, where the sum of all the elements are equal to 1. Solving for $\mathbf{l_i}$ gives:

$$\mathbf{l_i} = \mathbf{x_i}\mathbf{B}^{-1}. \quad (5)$$

4. *End-member mixing analysis (EMMA)*. EMMA was used to evaluate results from multiple solute tracers (Hooper et al., 1990; Christophersen et al., 1990). The five steps outlined by Christophersen and Hooper (1992) were followed: (1) Solutes that mix conservatively within the system were selected from linear plots of every pairwise combination of solutes (mixing diagrams); (2) A principal components analysis (PCA) was performed on the stream-water data, which include ($p > 2$) solutes, to determine the number of end members; (3) Potential end members were projected into the U-space defined by the PCA; (4) The set of end members whose orthogonal projections best bound the stream water observations were chosen and (5) EMMA was performed as described above to solve for the proportions, $\mathbf{l_i}$, using the orthogonal projections of the end members.

4. Results

4.1. Hydrometric observations

The summer of 1995 was drier than normal; mean daily streamflow during July in the Neversink River about 10 km from the study site was 0.8 mm/d (Firda et al., 1996) compared to a 43-year July mean of 1.1 mm/d. The throughfall amount for the five events studied during July 1995 ranged from 9.9 to 34.0 mm (Table 1), and average throughfall intensities ranged from 0.8 to 3.6 mm/15 min. The event of greatest intensity was on July 26, in which 21 mm of throughfall fell in 30 min. Peak runoff was more strongly related to throughfall intensity (average R^2 among the catchments = 0.64) than throughfall amount.

The hydrographs of the summer events exhibited a rapid response to rainfall (Fig. 2a). Time-to-peak ranged from 15 to 45 min in the smallest catchment and from 1 to 2 h in the largest catchment, depending on throughfall characteristics. Recession times ranged from 1.5 to 4.0 h in the smallest catchment, and from 3 to 6 h in the largest catchment. Steep recessions typically indicate rapid drainage either as overland flow or flow through macropores (Pearce and McKerchar, 1979), but overland flow was observed to be minimal during the monitored events.

The runoff coefficient, or the percentage of quickflow relative to net throughfall (QF/ThFall), represents the proportion of the catchment contributing to

Fig. 2. (a) Rainfall and runoff response during the study period for the largest catchment, (b) hillslope groundwater well response, (c) mean shallow soil water content response and (d) mean deep soil water content response.

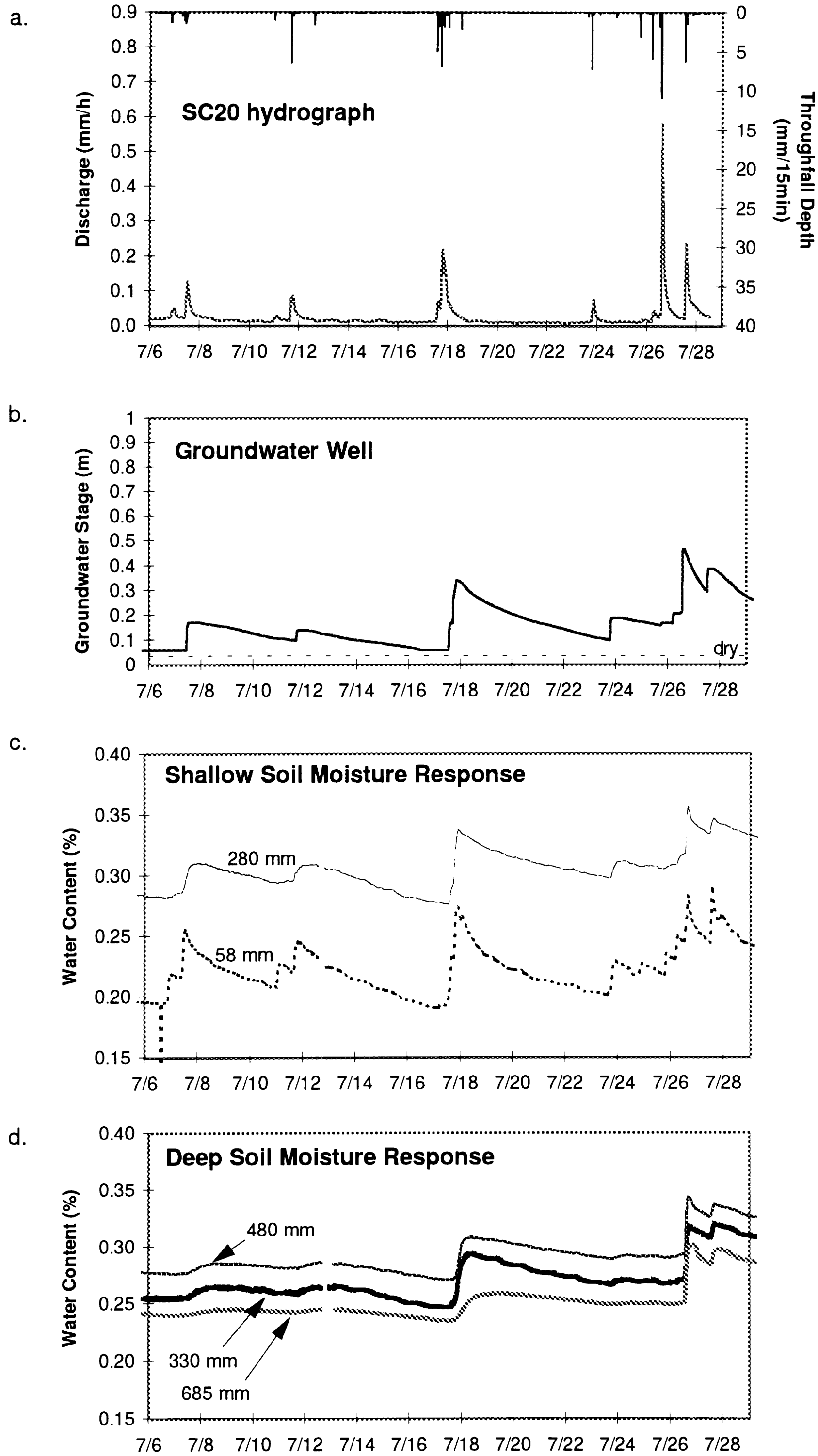
a.
SC20 hydrograph
Discharge (mm/h)
Throughfall Depth (mm/15min)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
5
10
15
20
25
30
35
40
7/6 7/8 7/10 7/12 7/14 7/16 7/18 7/20 7/22 7/24 7/26 7/28
b.
Groundwater Well
Groundwater Stage (m)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
dry
7/6 7/8 7/10 7/12 7/14 7/16 7/18 7/20 7/22 7/24 7/26 7/28
c.
Shallow Soil Moisture Response
Water Content (%)
280 mm
58 mm
0.40
0.35
0.30
0.25
0.20
0.15
7/6 7/8 7/10 7/12 7/14 7/16 7/18 7/20 7/22 7/24 7/26 7/28
d.
Deep Soil Moisture Response
Water Content (%)
480 mm
330 mm
685 mm
0.40
0.35
0.30
0.25
0.20
0.15
7/6 7/8 7/10 7/12 7/14 7/16 7/18 7/20 7/22 7/24 7/26 7/28

Table 2
Results from hydrometric, isotopic and chemical hydrograph separations for each catchment and for each event in order of throughfall intensity. Double dash (–) indicates insufficient data were available for the calculation

				Hydrometric		Two-component isotopic separation	Two-tracer three-component separation
Event	Catchment	Area (ha)	Time-to-peak (hrs)	Runoff coefficient (QF/Thfall) (%)	Channel area (saturated % of catchment)	Maximum event-water contribution (%)	Maximum O-horizon contribution (%)
July 26 event	SC20	161	1.00	4.2	0.25	49	35
	SC40	109	0.75	4.7	0.23	51	46
	SS20	51	0.50	2.7	0.21	56	69
	NS25	33	-	-	0.22	54	42
	DC57	24	0.25	0.6	0.09	53	31
	DC70	11	0.25	0.4	0.01	55	25
	DC28	8	-	-	0.14	62	75
July 27 event	SC20	161	1.50	4.9	0.25	37	16
	SC40	109	1.25	5.9	0.23	40	18
	SS20	51	1.25	2.9	0.21	47	34
	NS25	33	-	-	0.22	40	18
	DC57	24	0.25	0.5	0.09	34	10
	DC70	11	0.25	0.4	0.01	37	3
	DC28	8	0.25	1.0	0.14	47	-
July 17 event	SC20	161	1.50	2.9	0.25	29	15
	SC40	109	1.50	3.2	0.23	34	18
	SS20	51	1.25	1.5	0.21	-	-
	NS25	33	1.00	1.3	0.22	34	15
	DC57	24	0.25	0.3	0.09	30	10
	DC70	11	0.25	0.2	0.01	37	12
	DC28	8	0.25	0.8	0.14	42	36
July 23 event	SC20	161	2.25	1.8	0.25	24	-
	SC40	109	2.00	2.2	0.23	16	-
	SS20	51	1.75	1.1	0.21	32	-
	NS25	33	1.00	2.2	0.22	23	-
	DC57	24	0.25	0.3	0.09	21	-
	DC70	11	0.25	0.1	0.01	24	-
	DC28	8	$<$ 0.25	0.6	0.14	30	-
July 7 event	SC20	161	2.25	3.2	0.25	11	-
	SC40	109	2.00	3.3	0.23	15	-
	SS20	51	2.00	1.3	0.21	39	-
	NS25	33	1.50	1.3	0.22	39	-
	DC57	24	-	-	0.09	-	-
	DC70	11	0.75	0.2	0.01	13	-
	DC28	8	0.75	0.8	0.14	24	-

stormflow (Taylor and Pearce, 1982). Runoff coefficients ranged from 0.1% to 5.9% (Table 2) and are low in relation to values reported by Dunne (1978) for other forested sites in the northeastern United States. The runoff coefficients, however, were found to be an order of magnitude greater than the proportion of the catchment known to be saturated, as determined from the estimated surface area of the stream channel (Table 2). Direct precipitation onto saturated areas was probably not the dominant contributor to stormflow because overland flow and an expanding variable – source area in the near stream zone were observed

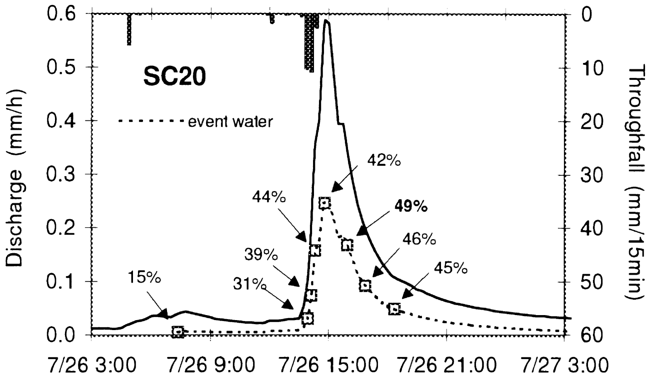

Fig. 3. Estimated event water contributions for the July 26 event at SC20.

to be minimal in extent even during the most intense events. A groundwater table developed quickly above the soil–bedrock interface on the hillslope in response to precipitation (within 15 to 60 min) and declined slowly over the next few days (Fig. 2b). Maximum water-table rise ranged from 0.05 to 0.3 m above the bedrock depending on throughfall intensity. The peak water-table elevations after most events were maintained for 2 to 11 h, and then declined at an average rate of 26 mm/d. The monitoring well became dry during the summer only after 7-day periods of no precipitation.

Water content in the shallow soil horizons (as measured by the TDR response) increased more quickly and to a greater extent than in the deeper soil horizons (Fig. 2c and 2d) for all but the most intense event on July 26 when the water content of the entire soil profile increased by 5%. Water content recession curves for the shallow soils (58 and 280 mm) had steeper slopes than the deeper soils (330 to 685 mm). This indicated more rapid drainage from the shallower soils than from the deeper soils where water tended to remain in storage due to the low gradient of the underlying bedrock surface. Diurnal decreases of < 0.005 (or 0.5%) in water content were observed at all but the 685 mm depth.

During the sampling period, zero-tension pan lysimeters collected water only in response to rain events, and the volume of water collected in the lysimeters was related to precipitation amount. The pan lysimeters in the O-horizon were more likely to collect water than pan lysimeters in the B- and C-horizons. Those in the B-horizon collected very little water, and those in the C-horizon collected either little or no water at some sites, or completely filled with water at other sites. Therefore, water from completely filled C-horizon lysimeters was considered to result from the rising water table overtopping the lysimeter collector, representing transient hillslope groundwater.

Table 3
End member chemistry for the July 26 and July 17 events used for separation calculations. Mean values with standard deviations below in parentheses. Mean values for soilwater samples weighted by lysimeter volume

	$\delta^{18}O$ (‰)	DOC (μmol/L)	SO_4^{2-} (μmol/L)	Cl^- (μmol/L)
26-Jul				
ThFall	−4.03	448.3	43.8	6.7
	(0.73)	(118.40)	(1.75)	(1.82)
O-hrz	−4.74	2090.1	50.0	8.2
	(1.42)	(884.04)	(7.34)	(2.55)
B-hzn	−7.48	356.7	50.6	15.6
	(2.10)	(252.00)	(4.20)	(5.50)
C-hzn	−8.30	338.2	51.8	16.0
	(1.40)	(165.80)	(5.50)	(4.40)
GW	−9.85	58.1	61.0	17.0
	(0.22)	(41.54)	(2.75)	(1.26)
Seeps	−10.02	47.9	62.8	17.5
	(0.13)	(28.70)	(2.70)	(1.48)
17-Jul				
ThFall	−5.27	448.3	39.1	5.2
	(0.25)	(118.40)	(1.91)	(0.43)
O-hrz	−6.36	2172.0	47.2	10.9
	(0.22)	(840.11)	(12.25)	(3.52)

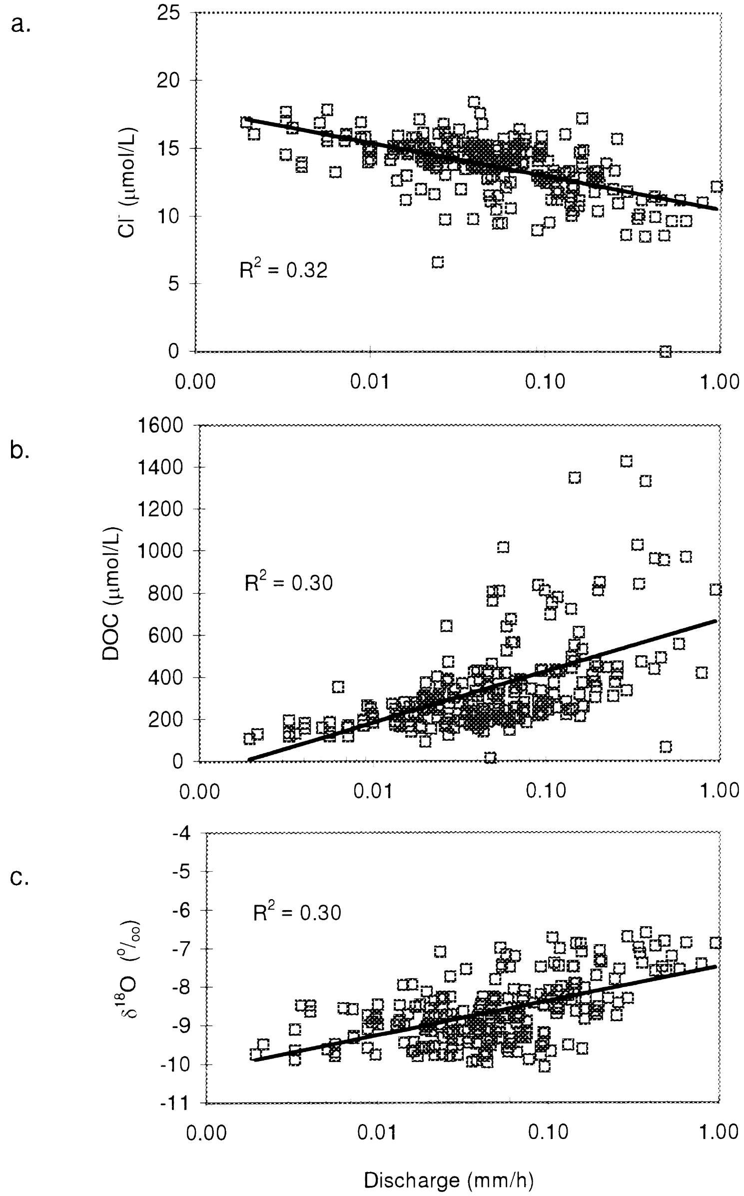

Fig. 4. Concentration-discharge relationships for (a) Cl^-, (b) DOC and (c) $\delta^{18}O$. Stormflow samples during July 1995 from all seven catchments are included.

4.2. Two-component isotopic hydrograph separation

Estimated maximum event-water contributions to stormflow ranged from 49% in the largest catchment to 62% in the smallest catchment during the event of greatest intensity on July 26 (Table 2). These maximum contributions were found to increase significantly with throughfall intensity for the five summer storms ($p < 0.001$, $R^2 = 0.69$) and typically occurred just after peakflow (Fig. 3) in most catchments where post-peak samples were obtained, for all but the event of lowest intensity.

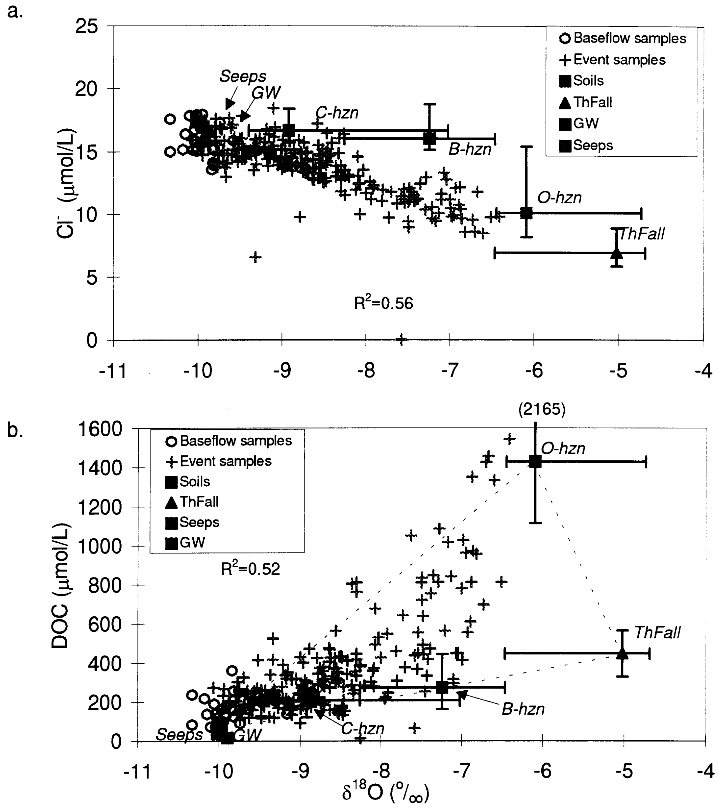

Fig. 5. Mixing diagrams for (a) $\delta^{18}O$ and Cl^- and (b) $\delta^{18}O$ and DOC. Medians of the end-members for all events combined are plotted with 25 and 75 percentile error bars.

A potential weakness of the two-component method is the assumption of no contribution to streamflow from pre-event soil water. Soil water probably does not contribute directly to baseflow, but may become mobilized during an event (Bazemore et al., 1994). The isotopic composition of soil water from the O- , B- , and C-horizon lysimeters was different from both baseflow and event water (Table 3), and $\delta^{18}O$ decreased with depth. Mobilization of this soil water and its subsequent contribution to stormflow would result in an overestimation of the event-water contribution.

The estimated uncertainty in the computed event and pre-event water fractions from Eq. (2) was found to range between 2.4% and 4.1% for all catchments and all events. Estimated uncertainty in the event contributions to stormflow in all of the catchments on July 26 ranged from 2.7% to 3.2%.

4.3. Solute tracer results

1. *Chloride* The concentration of Cl^- in each of the catchments was inversely related to both stormflow discharge and $\delta^{18}O$ for all analyses of event samples ($R^2 = 0.32$, $p < 0.001$, $n = 220$; $R^2 = 0.56$, $p < 0.001$, $n = 228$, respectively) (Figs. 4a and 5a). A strong linear dilution trend towards the throughfall component is apparent when the throughfall, soil water, groundwater, and seep-water sources are included on a bivariate plot of Cl^- concentration and $\delta^{18}O$ for event samples from all catchments. Stream $\delta^{18}O$ also increased with discharge ($R^2 = 0.30$, $p < 0.001$, $n = 220$) and results of a two-component hydrograph separation with Cl^- rather than $\delta^{18}O$ were similar to those results reported for $\delta^{18}O$.
2. *Dissolved Organic Carbon (DOC)* Generally, the concentration of DOC in each of the catchments

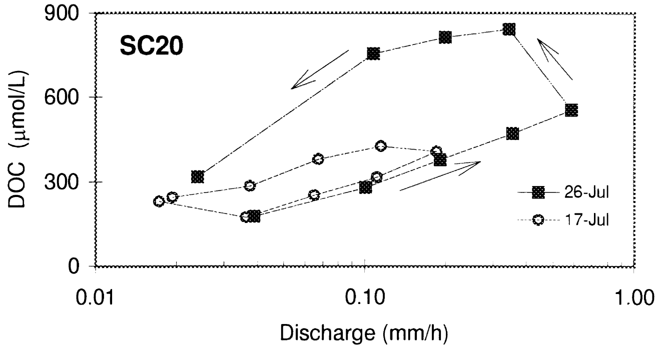

Fig. 6. DOC changes in stormflow for July 26 and July 17 events for SC20. DOC was lower on the rising limb and higher on the failing limb in each catchment, as shown with arrows.

increased with stormflow discharge ($R^2 = 0.30, p < 0.001, n = 219$) (Fig. 4b). DOC concentrations were consistently lower on the rising limb of the hydrograph than those on the recession limb in each of the catchments, however, except for DC70 (Fig. 6). The greatest DOC concentrations in stormflow were immediately after peakflow.

DOC concentrations were correlated with δ^{18}O ($R^2 = 0.52, p < 0.001, n = 227$). The mixing diagram of DOC and δ^{18}O (Fig. 5b) shows the influence of three components – throughfall, O-horizon soil water, and near-stream groundwater, which bound most of the event samples. The DOC concentrations and δ^{18}O of B- and C-horizon soil water were too low to explain the concentrations observed in stormflow. The water from seeps had similar concentrations to those of near-stream groundwater, but the discharge of seeps does not generally increase significantly during summer storms (Burns et al., 1998).

4.4. Two-tracer three-component hydrograph separation with ^{18}O and DOC

Because throughfall, O-horizon, and groundwater end-members bound the streamwater samples in the δ^{18}O and DOC mixing diagram (Fig. 5b), their relative contributions to each stormflow sample can be estimated (Fig. 7). The groundwater component generally dominated the hydrograph in each of the subcatchments, but the throughfall and O-horizon contributions were also significant contributors to stormflow. For example, the maximum O-horizon contributions ranged from 25% to 75% among the catchments for the July 26 event, whereas the

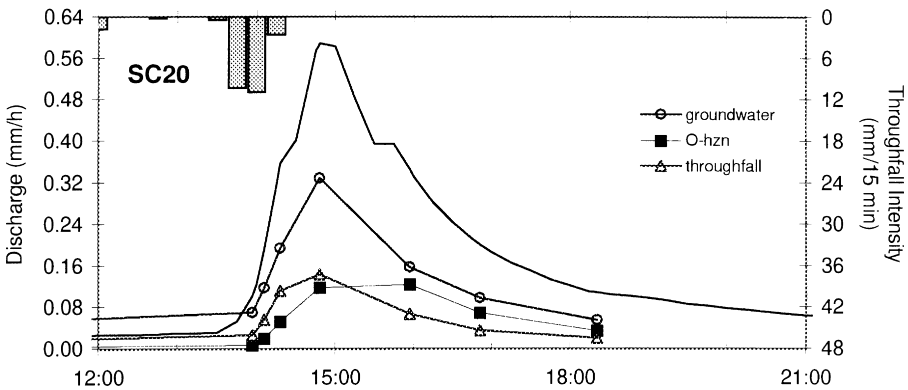

Fig. 7. Estimated groundwater, O-horizon and throughfall contributions from the two-tracer three-component separation with DOC and δ^{18}O for SC20 during the July 26 event.

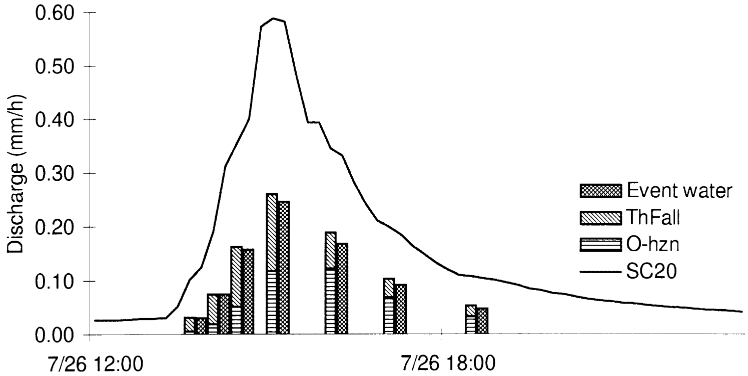

Fig. 8. Comparison of estimated event water contributions from the two-component isotopic separation and the combined estimated throughfall and O-horizon contributions from the two-tracer three-component separation for the same samples from SC20 on July 26.

minimum groundwater contributions ranged from 25 to 45% for this event. Maximum throughfall and groundwater contributions occurred at the same time as peak runoff, and dominated the rising limb of the hydrograph. The maximum O-horizon contribution to stormflow, however, occurred after peak runoff and played a greater role in the recession limb of the hydrograph, when groundwater and throughfall contributions were declining. This trend was consistent in each of the catchments, except DC70.

Estimated groundwater contributions were similar to the estimated pre-event water contributions from the two-component separation. The O-horizon and throughfall contributions together accounted for the estimated event water contributions from the two-component isotopic separation for each individual sample of the July 26 event in all catchments, to within an average of 4.0% (sd = 3.8%) (Fig. 8).

4.5. End-member mixing analysis (EMMA)

For the EMMA analysis, $\delta^{18}O$, DOC, Cl^-, and SO_4^{2-} were chosen because of their consistent and similar response to events in the streams. $\delta^{18}O$ and DOC concentrations consistently increased in streamflow in response to rain events while Cl^- and SO_4^{2-} concentrations consistently decreased. Results from the PCA for all stream water data (baseflow and events) showed that 92% of the variability in these samples could be explained by two principal components, implying that at least three end-members were required to explain streamwater response (Christophersen and Hooper, 1992). The chemical and isotopic composition of end members presented in this analysis is summarized in Table 3.

When the streamwater and end-member data were projected into the U-space defined by the streamwater data (Fig. 9a), the seepwater and groundwater samples plotted similarly. Baseflow samples plotted consistently close to the seep and groundwaters, and towards the C-horizon (transient groundwater) at times of higher baseflow. Stormflow samples, however, could not be explained by these groundwaters alone. Although the median values for the throughfall and O-horizon end-members did not sufficiently bound the stormflow data, the extreme values of each end-member did explain almost all of the variability in stormflow.

The actual percent contributions to flow attributable to each of the end members were not calculated due to the great variability in the characterization of the O-horizon and throughfall end members. Samples that fall outside the widest mixing triangle defined by these end-members may be due to either an insufficient characterization of the end-members, inclusion of DOC and SO_4^{2-}, which may not be sufficiently conservative tracers, or may be indicative of a more complex mixing of components.

A consistent trend among the stormflow data for each of the catchments was observed in the end-member plots (Fig. 9b and 9c): (1) at the start of the event, streamflow samples were close to the base-flow and groundwater samples; (2) during the rising limb of the hydrograph, samples began to move

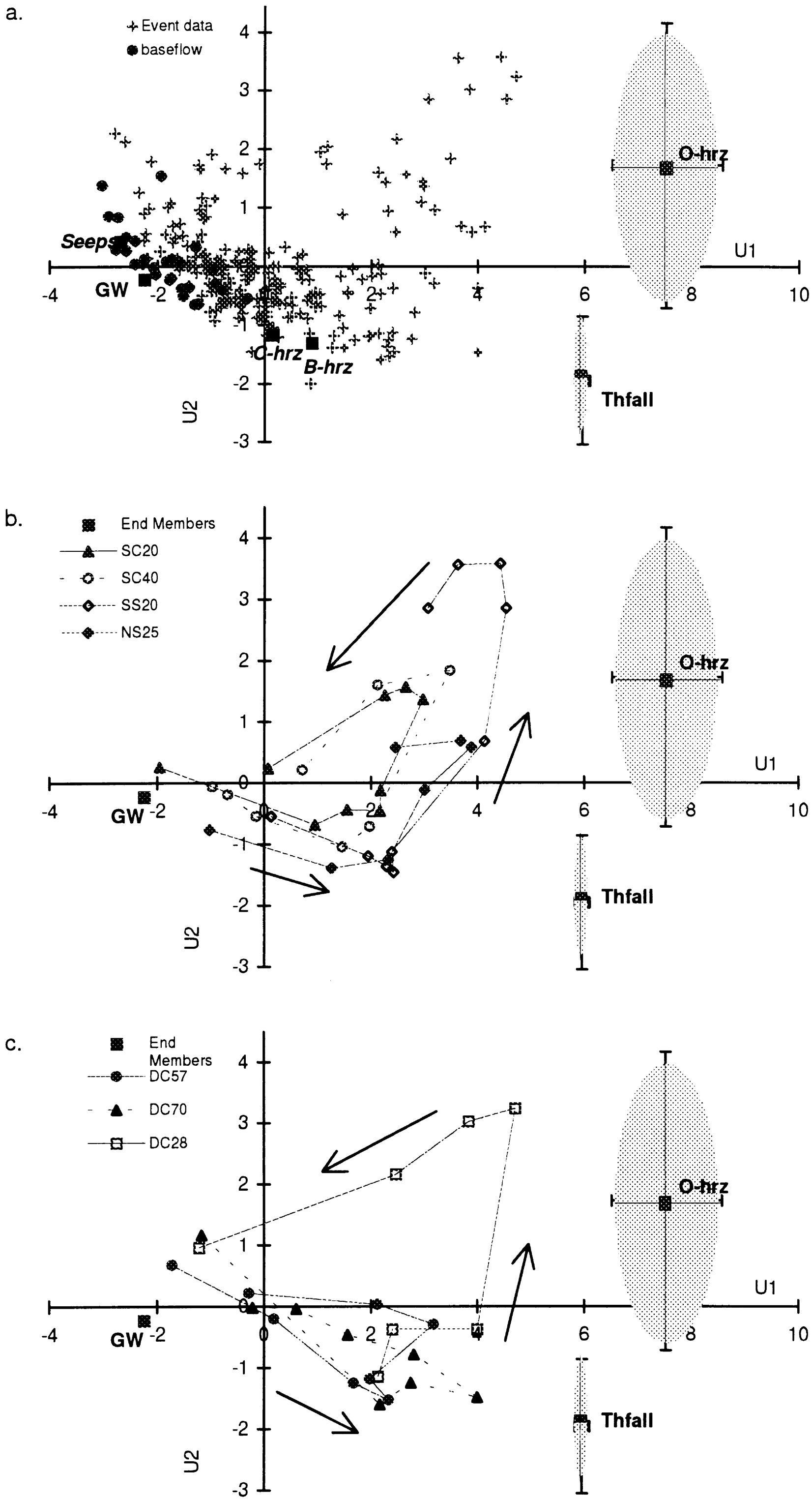
a.
Event data
baseflow
Seeps
GW
C-hrz
B-hrz
O-hrz
Thfall
U1
U2
b.
End Members
SC20
SC40
SS20
NS25
GW
O-hrz
Thfall
U1
U2
c.
End Members
DC57
DC70
DC28
GW
O-hrz
Thfall
U1
U2

Table 4
P-values for the relations between stormflow contribution and catchment size

	Hydrometric		Isotopic separation	Two-tracer three-component separation
	Peak runoff (mm)	QF/thfall (%)	Peak event water contribution (%)	Peak O-horizon contribution (%)
Relation with increasing catchment area	Increase	Increase	Decrease	No change
July 26 event	0.035	0.014	0.022	0.769
July 27 event	0.039	0.008	0.320	Na
July 17 event	0.017	0.003	0.097	0.770
July 23 event	0.105	0.055	0.210	Na
July 7 event	0.047	0.003	0.170	Na

towards the throughfall component; (3) after the peak of the hydrograph, samples moved towards the O-horizon component; (4) during the latter part of the recession limb, samples returned to the original base-flow conditions. This trend, illustrated with four tracers, was similar to that of the two-tracer three-component separation, where estimated O-horizon contributions were found to play a greater role in hydrograph recession. Stormflow samples did not plot close to the throughfall and O-horizon end members, an indication of groundwater dominance that was observed in both the two-tracer three-component separation and the two-component isotopic separation.

4.6. Catchment size

The hydrometric evidence indicated that catchment size affected the runoff response. Peak runoff per unit area (mm/h) and the runoff coefficient (QF/Thfall) increased significantly with increasing catchment size (Table 4).

The maximum event-water contribution to stormflow decreased with increasing catchment size according to the results from the two-component isotopic separation (Table 4). This relation was statistically significant only for the most intense event on July 26, however ($p = 0.023$). No relation between the size of the catchment and the maximum O-horizon contribution was apparent in results from the two-tracer three-component separation with $\delta^{18}O$ and DOC (Table 4). Additionally, no relation between the size of the catchment and the extent to which stormflow was influenced by either throughfall or O-horizon water or both was apparent in the EMMA results.

5. Discussion

Each of the subcatchments within the Shelter Creek catchment responsed similarly to storm rainfall during the summer of 1995, an indication that similar mechanisms may be controlling runoff generation during this season. Each subcatchment had high event-water contributions to stormflow (49% to 62% for the most intense event) that could not be explained by the small surface-saturated area of the catchment observed during events. Maximum contributions from throughfall and an organic shallow-subsurface flow component were as high as 30% to 46% and 25% to 75% respectively, and together could account for the maximum event-water contribution for any sample collected. Pre-event water, or groundwater, also contributed significantly to stormflow in most of the subcatchments. The extent to which the flow

Fig. 9. End member mixing analysis with four tracers: (a) July 1995 event data with six possible end members. July 26 event data with bounding end members (b) for catchments SC20, SC40, SS20 and NS25 and (c) for DC57, DC70 and DC28. End member data are mean values for July 26 with 95% confidence intervals. Arrows indicate sequence of samples through the hydrograph.

components contributed to stormflow varied among catchments as a function of drainage area.

The following discussion evaluates: (1) the role of event water in storm runoff, (2) the evidence for a transient O-horizon subsurface flow component that contributes to runoff, and (3) the effect of catchment size on the components of storm runoff.

5.1. The role of event water

Summer storm runoff in all of the catchments was characterized by high event-water contributions related directly to the average rainfall intensity. These high event-water contributions were indicated by both the δ^{18}O and Cl^- responses in stormflow. The negative correlation between Cl^- and δ^{18}O ($R^2 = .56$) in streamflow indicated a strong dilution trend towards the throughfall component (Fig. 5a). Chloride, however, was not as strongly correlated with discharge ($R^2 = 0.32$) (Fig. 4a), indicating that dilution of stormflow was more closely related to the timing of the contribution of the event-water component to stormflow than simply by the volume of discharge in the stream channel. In most of the catchments, the maximum event-water contributions occurred immediately after the hydrograph peak.

Overland flow and saturated overland flow were observed to be minimal in extent, and throughfall directly on surface-saturated stream channel areas was insufficient to account for the event-water contributions. The timing of the maximum event-water contribution indicates that the calculated event-water contributions were not related to direct precipitation on the stream channel, but rather to an alternative delivery mechanism. Some researchers consider it unlikely that throughfall infiltrating the soil can reach the stream channel without altering its chemical or isotopic composition (Pilgrim et al., 1979; Bazemore et al., 1994). If true, then an additional source of water with an isotopic signature similar to that of throughfall must have contributed to summer storm runoff. This conclusion however, is a violation of the assumptions made in separating runoff into event and pre-event water (Sklash and Farvolden, 1979).

The size of the event-water component may have been overestimated due to the mobilization of soil water. But if the event-water component includes both channel precipitation and a mixture of event and soil water flowing through or directly below the shallow organic soil horizon (Wels et al., 1991), then this redefined ''event'' water component may be underestimated (Robson et al., 1992). Solution to this problem requires knowing the extent that flow through the soil was affected by the throughfall component and pre-event soil water. Throughfall and O-horizon contributions determined from the separation with δ^{18}O and DOC, however, could together account for the event-water contribution to within an average of 4.0% (sd = 3.8%). The event-water component may therefore, consist of both channel throughfall and flow through the O-horizon.

Another explanation for the high event-water contribution is that the expansion of the channel area was underestimated. The steeply incised stream channels do not allow for significant channel area expansion and observations of the channel area during event sampling did not indicate that the near-stream saturated zone expanded in size. These observations from a period of high pre-storm moisture deficits indicate that the combined hydrometric–isotopic–geochemical data can be explained by a large contribution to stormflow from a shallow and rapid subsurface flow pathway.

5.2. Evidence of a rapid shallow subsurface flow component

The steep rising and recession limbs of the stormflow hydrographs indicated a rapid flowpath to the stream channel. Because overland flow was minimal, rapid flow through a macroporous medium was inferred, that may include macropores (Beven and Germann, 1982), cracks in the soil (McDonnell, 1990), or soil layers of differing hydraulic conductivity (Chappell et al., 1990; McDonnell et al., 1991). This inference is supported by the sound of water flowing during precipitation events immediately under the organic-covered rocky overburden common throughout the Catskills (P. Murdoch, personal communication). The inability of throughfall on the saturated channel area to fully account for the event-water contributions estimated from the two-component isotopic separation suggests a contribution from a source other than throughfall, but with an isotopic signature similar to throughfall. Only the water collected from the O-horizon had a δ^{18}O composition heavy enough to explain the isotopic response in stormflow.

The strong correlation between DOC concentrations and $\delta^{18}O$ (Fig. 5b) in stormflow is also consistent with a large contribution from the O-horizon, which has high $\delta^{18}O$ and high DOC concentrations. Transient groundwater (C-horizon soil water) did not have high enough DOC concentrations to explain the response of DOC concentrations during stormflow. DOC concentrations, like those of Cl^-, were more strongly correlated with $\delta^{18}O$ than discharge (Figs. 5b and 4b), indicating that the contribution of DOC to stormflow was more closely related to the timing of the O-horizon contribution than to discharge in the stream channel.

Concentrations of DOC were consistently lower on the rising limb than on the recession limb of the hydrograph (Fig. 6), opposite to that observed in Maimai, New Zealand (Moore, 1989) and in a small hardwood catchment in Massachusetts (McDowell and Fisher, 1976) where DOC concentrations were higher on the rising limb and lower on the recession limb. That pattern was attributed to higher DOC concentrations in throughfall than in streamwater (Moore, 1989), and to the mobilization of DOC or particulate organic matter in the stream bed through increased turbulence associated with increased discharge (McDowell and Fisher, 1976). The opposite pattern observed in this study can be explained by a large contribution of O-horizon soil water that was slightly delayed from the hydrograph peak, and which contributed more greatly to stormflow during the recession than during the rising limb of the hydrograph.

The O-horizon component is postulated to occur as lateral flow above the mineral soil surface as described by McDonnell et al. (1991). The high contrast in hydraulic conductivity between the porous organic material and the mineral horizon promotes lateral flow during precipitation events (Chappell et al., 1990). Water content in the upper soil profile increased and decreased more rapidly and to a greater extent than the water content in the deeper soil in response to rain events, supporting the shallow lateral-flow hypothesis. The shallow soil water, however, may have drained either in a lateral direction toward the stream channel or in a vertical direction deeper in the soil. But water from the upper soil layer that was distinct from deeper soil water accounted for the response of DOC concentrations and $\delta^{18}O$ in stormflow, suggesting the importance of lateral flow to the stream from the upper soil layer.

Bypass flow to bedrock is inferred from the rapid response of the water table on the hillslope relative to the delayed response of water content in the mineral soil immediately above the water table. Groundwater levels, however, did not increase sufficiently to reach the organic horizon (increasing only 0.05–0.3 m in the 1–1.5 m soil) as might be expected in a transmissivity feedback process (Bishop et al., 1990). Furthermore, the bedrock surface at which the water table develops is effectively horizontal, decreasing the likelihood of subsurface flow induced by the topography of the bedrock surface as observed by McDonnell et al. (1996).

5.3. Effect of catchment size on flow sources and flow components

Peak runoff increased significantly with drainage area in these small Catskill catchments (0.08 to 1.61 km^2) (Table 4). This finding is consistent with that of Renard (1977) that runoff increases with catchment size in humid climates. In data compiled by Dunne (1978), however, runoff decreased with drainage area in catchments dominated by either Hortonian overland flow or subsurface flow.

Runoff coefficients (QF/ThFall) also increased significantly with catchment size during the storm events in this study (Table 4). In contrast, runoff coefficients (QF/Rainfall) from data compiled by Dunne (1978) decreased with increasing catchment area.

Estimated event-water contributions at the hydrograph peak as indicated by the two-component separation decreased with increasing catchment area (Table 4), whereas pre-event water contributions increased. Because pre-event water was considered to be mainly groundwater, a downstream increase in groundwater contribution to stormflow is indicated. The greatest contribution of event water to stormflow was in the smaller catchments where the near-stream groundwater reservoir is probably smaller. This is the opposite of that observed at Maimai, New Zealand, where the higher event contributions in larger catchments were attributed to a greater proportional area of saturated valley flow that provided greater saturated overland flow (Pearce, 1990). The size of the saturated areas in this study did not increase measurably during events, and saturated overland flow did not contribute greatly to summer stormflow. This suggests a fundamental difference exists between the humid Maimai site and the dry summer conditions studied in these small Catskills catchments.

Event water contributions to stormflow consisted of a channel throughfall and a shallow subsurface flow component. The maximum event-water contributions to stormflow decreased with increasing catchment area, but the maximum contribution from shallow subsurface flow (O-horizon) was not influenced by catchment area (Table 4). The estimated shallow subsurface contributions were greatest for catchments DC28 and SS20, which are characterized by areas of low slope just upstream of the stream gages. The shallow subsurface contributions to stormflow may be affected more strongly by physiographic and/or topographic characteristics than by catchment area. Further research relating stormflow end-member contributions to topography is required to test this hypothesis.

6. Summary and Conclusions

Summer stormflow was characterized by rapid increases and decreases in streamflow. The estimated event-water contributions to peakflow from a two-component isotopic separation were as high as 49% to 62% for the event of greatest intensity, and could not be accounted for by direct throughfall onto saturated areas. Two-tracer three-component separations (with δ^{18}O and DOC) and EMMA indicated three end members that contributed to summer stormflow-channel throughfall, O-horizon soil water, and near-stream groundwater. Channel throughfall and O-horizon contributions to stormflow together approximated the estimated event-water component. Results from EMMA showed a consistent progression of end member influence on stormflow; first from throughfall until the time of peakflow, then from O-horizon soil water immediately after the hydrograph peak, and finally from near-stream groundwater in the latter part of the recession curve. These results suggest rapid delivery of water through the shallow subsurface to the stream with a maximum contribution to stormflow during the hydrograph recession.

Peak runoff increased significantly with increasing catchment area, whereas the event-water contributions at the hydrograph peak decreased significantly with increasing catchment area for only the most intense rainfall event. Estimated O-horizon contributions at the hydrograph peak were not affected by catchment area.

This study is the first comprehensive test of the importance of event water, a rapid shallow flow component, and catchment size in summer stormflow. Previous studies of runoff generation in humid areas or under wet antecedent conditions have concluded that pre-event water and deeper flowpaths constitute the majority of stormflow response. These results indicate that event water is a major contributor to stormflow during dry conditions. Furthermore, a rapid shallow flow component is a major control of stormflow chemistry and isotopic composition. Additional processes remain to be studied at the hillslope scale to fully explain and understand the significance of these results. Further research into the relations between estimated end-member contributions to stormflow and catchment topographic parameters is necessary to fully describe stormflow generation as a function of catchment scale.

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