

Controls on old and new water contributions to stream flow at some nested catchments in Vermont, USA

James B. Shanley,^{1*} Carol Kendall,² Thor E. Smith,³ David M. Wolock⁴ and Jeffrey J. McDonnell⁵

¹ U.S. Geological Survey, Box 628, Montpelier, VT 05601, USA

² U.S. Geological Survey, 345 Middlefield Rd., Menlo Park, CA 94025, USA

³ U.S. Geological Survey, 361 Commerce Way, Pembroke, NH 03275, USA

⁴ U.S. Geological Survey, 4821 Quail Crest Place, Lawrence, KS 66049, USA

⁵ Department of Forest Engineering, Oregon State University, Corvallis, OR 97331, USA

Abstract:

Factors controlling the partitioning of old and new water contributions to stream flow were investigated for three events in four catchments (three of which were nested) at Sleepers River Research Watershed in Danville, Vermont. In the 1993 snowmelt period, two-component isotopic hydrograph separations showed that new water (meltwater) inputs to the stream ranged widely from 41 to 74%, and increased with catchment size (41 to 11 125 ha) (with one exception) and with open land cover (0–73%). Peak dissolved organic carbon concentrations and relative alkalinity dilution in stream water ranked in the same order among catchments as the new water fractions, suggesting that new water followed shallow flow paths. During the 1994 snowmelt, despite similar timing and magnitude of melt inputs, the new-water contribution to stream flow ranged only from 30 to 36% in the four catchments. We conclude that the uncommonly high and variable new water fractions in streamwater during the 1993 melt were caused by direct runoff of meltwater over frozen ground, which was prevalent in open land areas during the 1993 winter. In a high-intensity summer rainstorm in 1993, new water fractions were smaller relative to the 1993 snowmelt, ranging from 28 to 46%, but they ranked in the identical catchment order. Reconciliation of the contrasting patterns of new–old water partitioning in the three events appears to require an explanation that invokes multiple processes and effects, including:

1. topographically controlled increase in surface-saturated area with increasing catchment size;
2. direct runoff over frozen ground;
3. low infiltration in agriculturally compacted soils;
4. differences in soil transmissivity, which may be more relevant under dry antecedent conditions.

These data highlight some of the difficulties faced by catchment hydrologists in formulating a theory of runoff generation at varying basin scales. Copyright © 2002 John Wiley & Sons, Ltd.

KEY WORDS snowmelt; hydrograph separation; oxygen isotopes; DOC; new water; Vermont

INTRODUCTION

For much of the twentieth century, hydrologists have struggled to explain how water moves through the landscape to stream channels during rain and snowmelt events. Despite the common observance of rapid event-induced increases in stream discharge, the accumulating evidence from 20 years of isotopic studies has imposed the seemingly paradoxical constraint (Bishop, 1991) that the event hydrograph is dominated by pre-event water (Sklash and Folvolden, 1979; Genereux and Hooper, 1998). New findings and revised conceptualizations of catchment functioning have begun to unravel this paradox (e.g. McDonnell, 1990), as

* Correspondence to: James B. Shanley, U.S. Geological Survey, P.O. Box 628, Montpelier, VT 05601, USA. E-mail: jshanley@usgs.gov

Received 28 September 1999

Accepted 9 January 2001

outlined in reviews by Bonell (1993, 1998) and Buttle (1994), but much controversy remains (e.g. Buttle and Sami, 1992). Previous attempts to explain old and new water partitioning commonly have been based on interpretations of isotope dynamics at the small watershed or hillslope plot scale. Results were often subsequently generalized to other catchments or to a region (Sklash and Farvolden, 1979). In this study we take an alternative approach whereby we compare the isotopic response in nested and paired catchments of differing sizes and physical characteristics, and under different hydrological conditions, to deduce the factors that control old and new water partitioning in stream flow.

How do watershed characteristics affect old and new water fractions in stream flow? One intuitive factor that may explain new water inputs is topography (Wolock, 1995). Steep terrain promotes rapid runoff, yet isotopic studies have shown that even steep 'flashy' catchments are dominated by old water (Sklash *et al.*, 1986). Impermeable soil also may cause rapid runoff, although Bishop (1991) found that old water dominated stormflow in a Scottish catchment where impermeable subsoil restricted nearly all flow to the uppermost 200 mm of soil.

Dunne and Black (1970a,b) advanced the concept of saturation overland flow at Sleepers River, Vermont, site of the present study. Building on the partial area contribution theory of Betson (1964), Dunne and Black (1970b) concluded that stream flow was generated by direct precipitation on saturated areas, which expanded outward from the stream and into convergent hollows during events, as well as return flow from upslope that issued into the surface-saturated area. Precipitation or snowmelt directly on to saturated areas clearly moves to the stream as new water. Dunne and Black (1970b) implied that return flow also was new water, but recent isotopic studies at Sleepers River (Titus *et al.*, 1995; McGlynn *et al.*, 1999) indicate that return flow is a mixture of old and new water, and in fact is dominated by old water.

In addition to saturation overland flow, Dunne and Black (1971) also observed Hortonian overland flow on areas of concrete frost at Sleepers River. They viewed the areas of frozen ground as a separate category of contributing area that adds to contributions from surface-saturated areas. The effect of frozen ground in routing water rapidly overland has received considerable attention in western North America (Zuzel and Pikul, 1987; Seyfried and Flerchinger, 1994), Alaska (Kane and Stein, 1983), Sweden (Johnsson and Lundin, 1991), and the former Soviet Union (Shipak, 1969). Ground frost also has been documented in eastern North America (Sartz, 1957; Fahey and Lang, 1975), but there has been little study of its hydrological effects. Ground frost reportedly had a role in the great 1936 flood in New England (Diebold, 1938), and recently was shown to cause increased runoff during some rainstorms at Sleepers River (Shanley and Chalmers, 1999). In addition to contributing to snowmelt runoff flooding, ground frost may lead to contamination of surface waters if salt-laden highway runoff or fertilizer and manure applied during winter run off over frozen soil directly into streams.

In northern New York and New England and adjacent areas of Canada, half of the annual stream flow occurs in the 6-week period of spring snowmelt. Most of the annual recharge occurs during this period and groundwater rises to its highest level of the year. Contaminants are released from the snowpack and/or flushed from the surficial soil by meltwater, and may either infiltrate or travel directly to the stream. Isotopes and certain chemical tracers allow us to track the fate of these substances, and to partition meltwater between infiltration and runoff over saturated or frozen ground. The isotopic composition of runoff over frozen soil has rarely been investigated (Cooper, 1998).

In this paper we use a large isotopic data set, supplemented by chemical and hydrological measurements, to compare two snowmelt events and a summer rain storm in a set of four catchments at Sleepers River. Our isotopic data set, acquired from nested catchments sampled intensively during events, is one of the few such data sets in existence. Pearce (1990) measured δD at a smaller set of scales up to 100 ha, Brown *et al.* (1999) measured $\delta^{18}O$ during storm events in nested catchments up to 161 ha, and Sueker *et al.* (2000) reported isotopic data from snowmelt in several catchments, some of them nested, with areas of tens of square kilometres. We investigated controls on old and new water partitioning by the evaluation of factors that vary over space (terrain, soils and land cover) and factors that vary over time (antecedent moisture and ground frost), in the hope of gaining insight into runoff generation processes in an upland mid-latitude landscape.

SITE DESCRIPTION

Sleepers River Research Watershed is a 111-km² basin in rural north-eastern Vermont. It was founded in 1957 by the Agricultural Research Service (ARS), which established 17 stream gauging stations and 13 meteorological stations in diverse settings. In addition to the studies of Dunne and Black (1970a,b, 1971), ARS research at Sleepers River focused on differences in flow characteristics among the 17 gauged watersheds on the basis of: (i) soils (Comer and Zimmerman, 1969), (ii) differences in antecedent baseflow status (Engman, 1981) and (iii) elevational controls on precipitation quantity (DeAngelis *et al.*, 1984). In 1966, the National Weather Service (NWS) initiated snow hydrology research at Sleepers River, using an energy balance approach to model snowmelt runoff (Anderson, 1979). Snowmelt modelling was later continued by the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) in Hanover, NH. Since 1990, the U.S. Geological Survey (USGS), in cooperation with CRREL, has operated Sleepers River as one of the five Water, Energy, and Biogeochemical Budgets (WEBB) research sites of the USGS Global Change Hydrology programme (Lins, 1994; Shanley *et al.*, 1995c).

Four gauged catchments within the Sleepers River Research Watershed (Figure 1) were selected for intensive study. Three of the basins are nested; W-9, W-3 and W-5 progressively increase by an order of magnitude in area (Table I). Land use is a mixture of forest and dairy pasture, with percentage forest cover decreasing from W-9 (100%) to W-3 (80%) to W-5 (67%). The fourth catchment, W-2, is a small

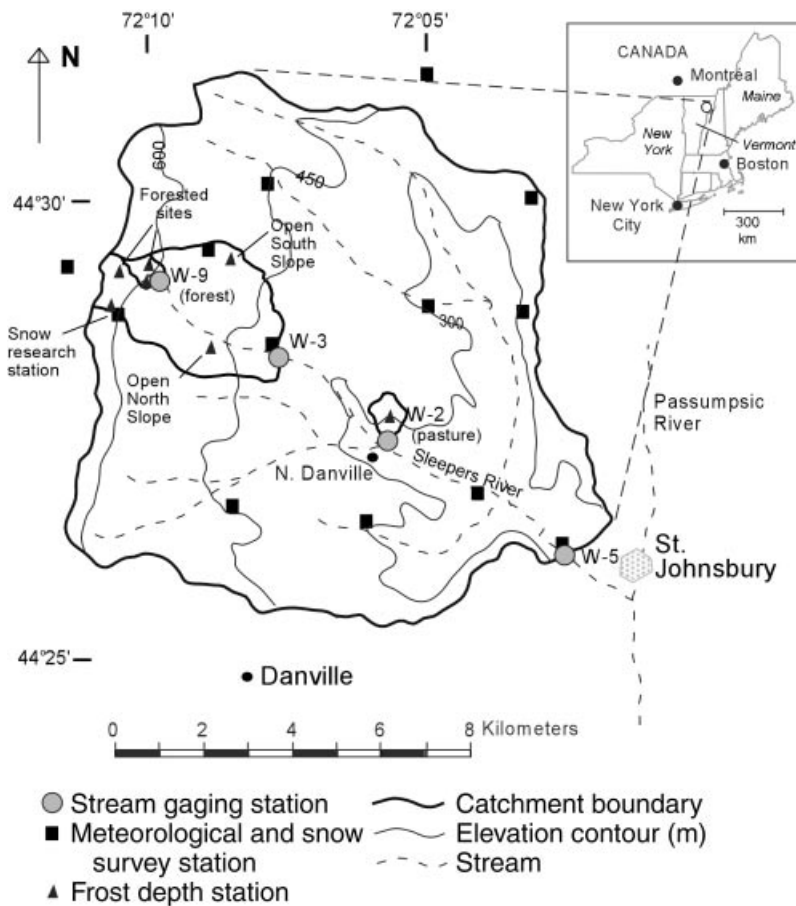


Figure 1. Map of Sleepers River Research Watershed

Table I. Comparison of physical characteristics for Sleepers River catchments

	W-9	W-3	W-5	W-2
Area (ha)	41	837	11 125	59
Minimum elevation (m)	519	353	195	285
Maximum elevation (m)	686	729	790	377
Forest cover (%)	100	80	67	27

agricultural site within W-5 that is only 27% forested. In the mid-1980s, drain tiles were installed at W-2 to increase usable pasture area by drying up the riparian zone. Groundwater discharges from the drain tiles year round.

Forested land at Sleepers River watershed is primarily northern hardwoods dominated by sugar maple, yellow birch, American beech and white ash. Conifers include balsam fir, red spruce, tamarack and white cedar. The open land is primarily hayfields and dairy pasture; about 1% of the basin is planted in corn. Land elevation ranges from 195 to 790 m. The Waits River Formation, a quartz-mica phyllite with beds of calcareous granulite, underlies 99% of the basin. A fine silty calcareous till overlies the bedrock to a depth of 1 to 3 m but locally is much thicker. Stream chemistry is primarily a calcium bicarbonate water from dissolution of calcite in the till and bedrock. Soils range from well-drained podzolic Distrochrepts and Fragiochrepts to poorly drained boggy Fragiaquepts (Comer and Zimmerman, 1969). Precipitation at mid-elevation averages somewhat more than 1000 mm annually; 25–30% falls as snow. Snow cover in upper elevations typically is present from mid-November to late April.

METHODS

Sampling and field measurements

The four study catchments were monitored intensively for chemistry and oxygen isotopes during the 1993 and 1994 snowmelt periods, and a 1993 summer storm. Precipitation quantity was recorded with shielded weighing bucket gauges at 13 sites in forest openings (Figure 1). Rain and snowfall events were differentiated through field notes from near-daily site visits. Snow depth and snow water equivalent (SWE) were measured at these sites weekly, and more frequently during active melt. Melt rates were calculated from changes in SWE. Wet-only precipitation was collected in a clearing near W-9 for chemical and isotopic analysis. Stream water in the four basins was sampled at intervals of 24 h or less during periods of active snowmelt, and 1 h or less during the summer storm, either manually or by automated samplers. Snow cores were obtained for chemical and isotopic analysis near the date of peak accumulation. Meltwater (and rain-on-snow drainage) was collected from four 0.5-m² plexiglas lysimeters placed on the forest floor before winter at various aspects within W-9. Snowmelt drained to 13-L containers and was sampled for $\delta^{18}\text{O}$ once or twice per day during active melt periods.

Soil water was collected by zero-tension lysimeters on a hillslope area within W-9. One lysimeter was under the forest floor at 50 mm depth and one was within the B-horizon at 400 mm depth. Soil water was sampled daily during active melt periods when sufficient volume was present. Thirteen shallow groundwater wells in W-9 were sampled approximately twice weekly during snowmelt periods. Ground frost depth was measured weekly at 36 points in both forested and open settings (Figure 1) using methylene blue solution in clear flexible tubing suspended vertically in the soil within PVC casing (Shanley and Chalmers, 1999); the solution excludes the blue upon freezing, precisely marking the frost line.

Laboratory analysis

An aliquot of each sample was sent to the USGS laboratory in Menlo Park, CA for $\delta^{18}\text{O}$ determination. The $\delta^{18}\text{O}$ values are reported in ‰ relative to VSMOW (precision $\pm 0.05\text{‰}$). Samples were filtered and analysed for major solutes and dissolved organic carbon (DOC) at the USGS laboratory in Troy, NY. Only alkalinity and DOC concentrations are reported here. Alkalinity (precision $\pm 10\%$) was determined from an unfiltered aliquot by Gran titration on an automatic titrator. The DOC concentration (precision $\pm 15\%$) was determined by ultraviolet persulphate oxidation with infrared detection on an aliquot filtered by 0.7- μm glass fibre membrane.

Data analysis

Two-component isotopic hydrograph separations using a constant composition groundwater and a variable composition meltwater were performed for each basin for the two snowmelt periods and the summer storm. The three-component separation method of DeWalle *et al.* (1988) could not be applied because the required survey of surface-saturated area was not possible with snow cover. Likewise, a classic three-component separation similar to Hinton *et al.* (1994) was not possible because soil water was not isotopically or chemically distinctive; shallow soil water from the O-horizon (50 mm depth) had an isotopic signal very similar to snowmelt water, and deeper soil water from the B-horizon (>400 mm depth) had an isotopic signal very similar to groundwater. Moreover, silica, the tracer of choice in many chemical hydrograph separations (Hooper and Shoemaker, 1986; Maulé and Stein, 1990; Hinton *et al.*, 1994) had nearly the same concentration in soil water and groundwater (Shanley *et al.*, 1995b).

The new and old water components of stream flow were calculated from the $\delta^{18}\text{O}$ of streamwater using meltwater or rain (for summer storm) at W-9 for new water $\delta^{18}\text{O}$ and pre-event stream water in each basin for old water $\delta^{18}\text{O}$. For snowmelt, the arithmetic average $\delta^{18}\text{O}$ from the four lysimeters at W-9 for each sampling date was used for the new water $\delta^{18}\text{O}$ basinwide. The $\delta^{18}\text{O}$ values of stream flow and snowmelt were linearly interpolated between sample times. The separation was performed at each inflection point on the hydrograph (approximately 50 points per day) to simplify the calculation of flow-weighted new and old water contributions. For the summer rain storm, $\delta^{18}\text{O}$ from the single event sample was used for the new water value. Smith *et al.* (in review) performed an error analysis on the isotopic hydrograph separation for the 1993 snowmelt at Sleepers River following the method of Genereux (1998). The uncertainty in the new water determination was less than 20% (at the 80% confidence level), and generally decreased as new water percentage increased.

RESULTS

Hydrology

Event Chronologies. In the winter of 1993, no appreciable snowpack developed until mid-January (Figure 2a), but thereafter the snowpack increased steadily to its maximum SWE of 241 mm in late March. The unusually long period of snow-free ground in early winter promoted deep soil frost development (Figure 2c). When the insulating snowpack is thin or absent, ground frost develops in open land preferentially to forests because night-time radiational cooling tends to be stronger, and soils in open land lack the thick organic surface that provides insulation in the forest (Dingman, 1975). Within the forest, coniferous areas are more susceptible to ground frost because their high interception rates limit snow accumulation. The 1994 snowpack developed in a more typical pattern starting in early December, and SWE reached 253 mm in late March (Figure 2b). These SWE maxima are about average for Sleepers River (Shanley *et al.*, 2000). Frost depth in 1994 was about one-half that in 1993 (Figure 2).

Snowmelt in both 1993 and 1994 occurred from late March to late April (Figure 2). There was about a two-week lag in snowpack ablation from low- to high-elevation sites, and the melt in 1994 was about a week

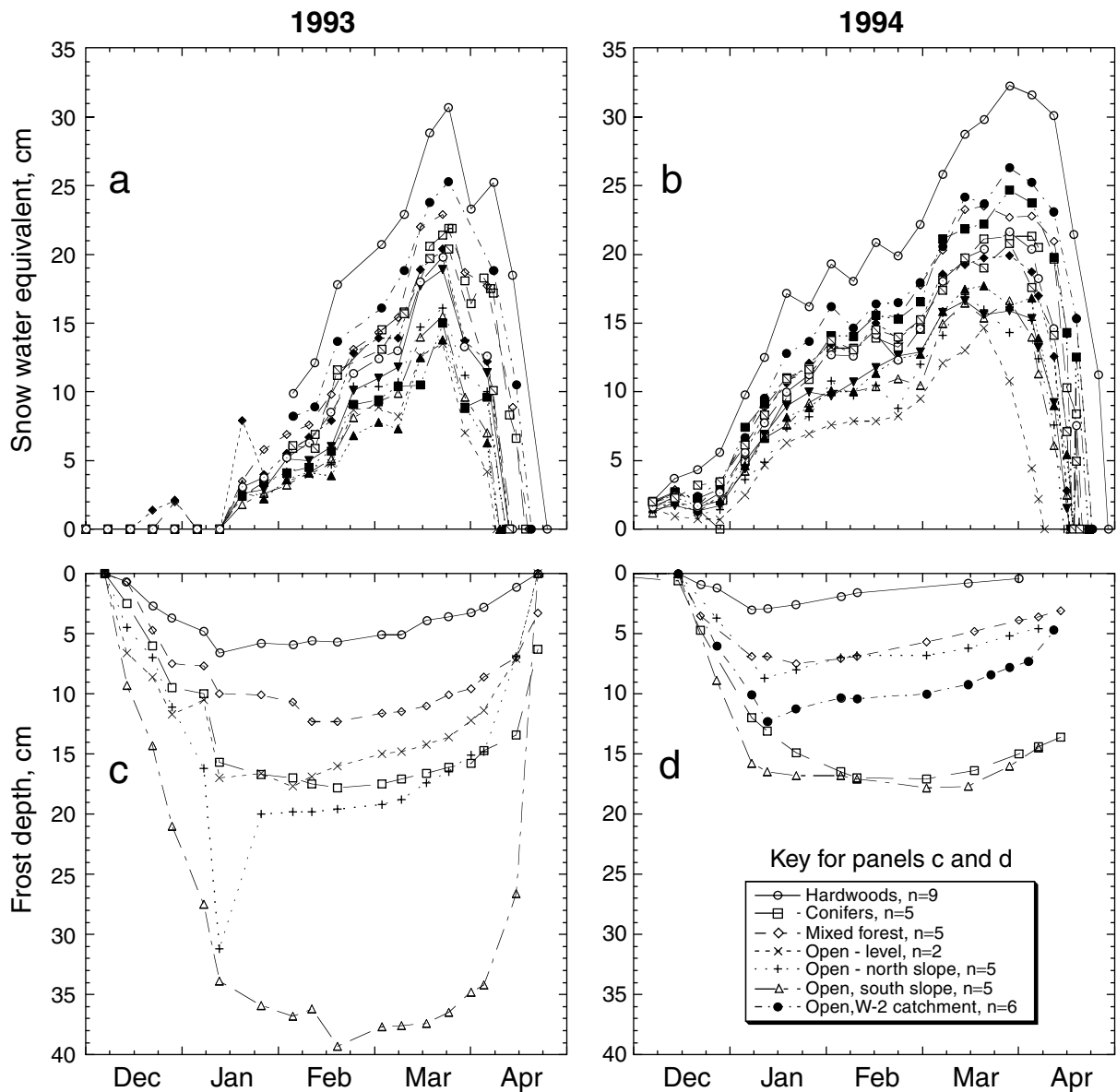


Figure 2. (a,b) Weekly snowpack water equivalent (13 sites) and (c,d) ground frost depth (6–8 sites) during the 1993 and 1994 winters. Each point is an average of five measurements for snow and two to nine measurements for frost

later than 1993 (Figure 3). Both years were marked by some large rain-on-snow events, but more rain fell during the 1994 melt (Table II). The August 1993 event was caused by a 4 h rainfall of 36 to 44 mm rain, varying by location.

Catchment runoff comparisons. There was strong similarity in the form of the snowmelt hydrographs in the three nested basins, illustrated by comparison of a series of diurnal melt cycles from 5 to 11 April in the 1993 melt (Figure 4). Even the largest basin, W-5, exhibited distinct diurnal flow cycles despite a slight lag to peak flow owing to travel time. The small agricultural W-2 catchment differed most from the other catchments by

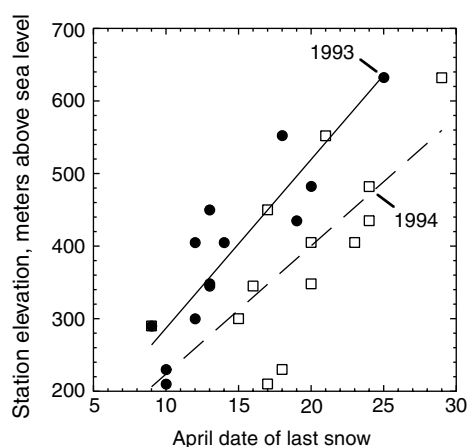


Figure 3. Date of final snowpack ablation, by elevation of measurement site, 1993 and 1994 winters

Table II. Hydrological inputs, outputs and runoff ratios for the three events, and recession constants during the 1993 snowmelt. Snowmelt events from 21 March through 22 April, both years (these dates give matching pre-melt starting flows and matching recession limb flows for the two years at all the catchments except W-2, where the recession flow remained higher in 1994). Meltwater input computed as difference between starting and ending SWE (all values in millimetres unless indicated otherwise; SWE, snow water equivalent)

	W-9	W-3	W-5	W-2
Snowmelt 1993:				
SWE—start	241	165	156	147
SWE—end	66	39	21	1
Meltwater input	175	126	135	146
Rain input	92	82	74	66
Total input	267	208	209	212
Runoff	229	174	163	144
Runoff ratio (%)	86	83	78	60
Snowmelt 1994:				
SWE—start	256	240	211	182
SWE—end	108	65	36	5
Meltwater input	148	175	175	177
Rain input	156	145	136	130
Total input	304	320	311	307
Runoff	204	169	162	108
Runoff ratio (%)	67	53	52	35
Summer storm:				
Rain input	36	38	40	44
Runoff	2.7	2.9	3.5	2.1
Runoff ratio (%)	7.6	7.6	8.7	4.7
Recession constant: ^a				
1–5 April 1993 (day ⁻¹)	0.27	0.73	1.2	3.6

^a Calculated from Nathan and McMahon (1990); $q_t = q_p e^{(-kt)}$ where q_t is the flow at time t during recession, q_p is the flow at peak, t is time, and k is the recession constant.

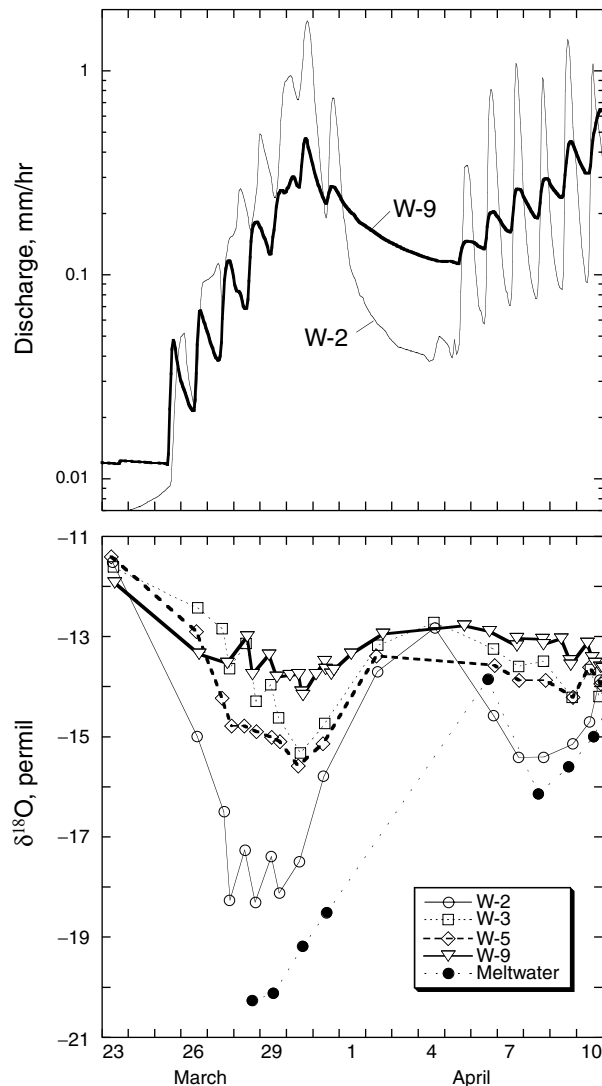


Figure 4. Stream flow (W-2 and W-9) and stream water $\delta^{18}\text{O}$ in the four catchments during the early part of the 1993 snowmelt. Meltwater $\delta^{18}\text{O}$ from W-9. Daily melt cycle stream flow hydrographs at W-3 and W-5 (omitted for clarity) were intermediate between W-2 and W-9 in amplitude (see Figure 5)

its more flashy diurnal responses and more complete return to base flow. Diurnal peak amplitudes increased in the order $W-9 < W-3 < W-5 \ll W-2$. Flow recession constants (Nathan and McMahon, 1990) calculated for the cold period from 1 to 5 April (Figure 4) followed the identical order (Table II), indicating that streams with the highest peak specific discharges had the fastest recessions. The watershed remained entirely snow-covered during the preceding late March snowmelt event (Figure 3), so differences in recession constants were probably not the result of differential retention of meltwater in the snowpack. Although total water input was greater in the 1994 snowmelt, stream hydrographs had a smaller diurnal range in flow compared with those in 1993, i.e. they were less flashy (Figure 5). Overall runoff was slightly less in 1994 than 1993, despite the higher inputs, implying that more water entered subsurface storage in 1994. The decrease in runoff in 1994 was more significant at W-2 (Table II). In the 1993 summer storm, which occurred under dry antecedent

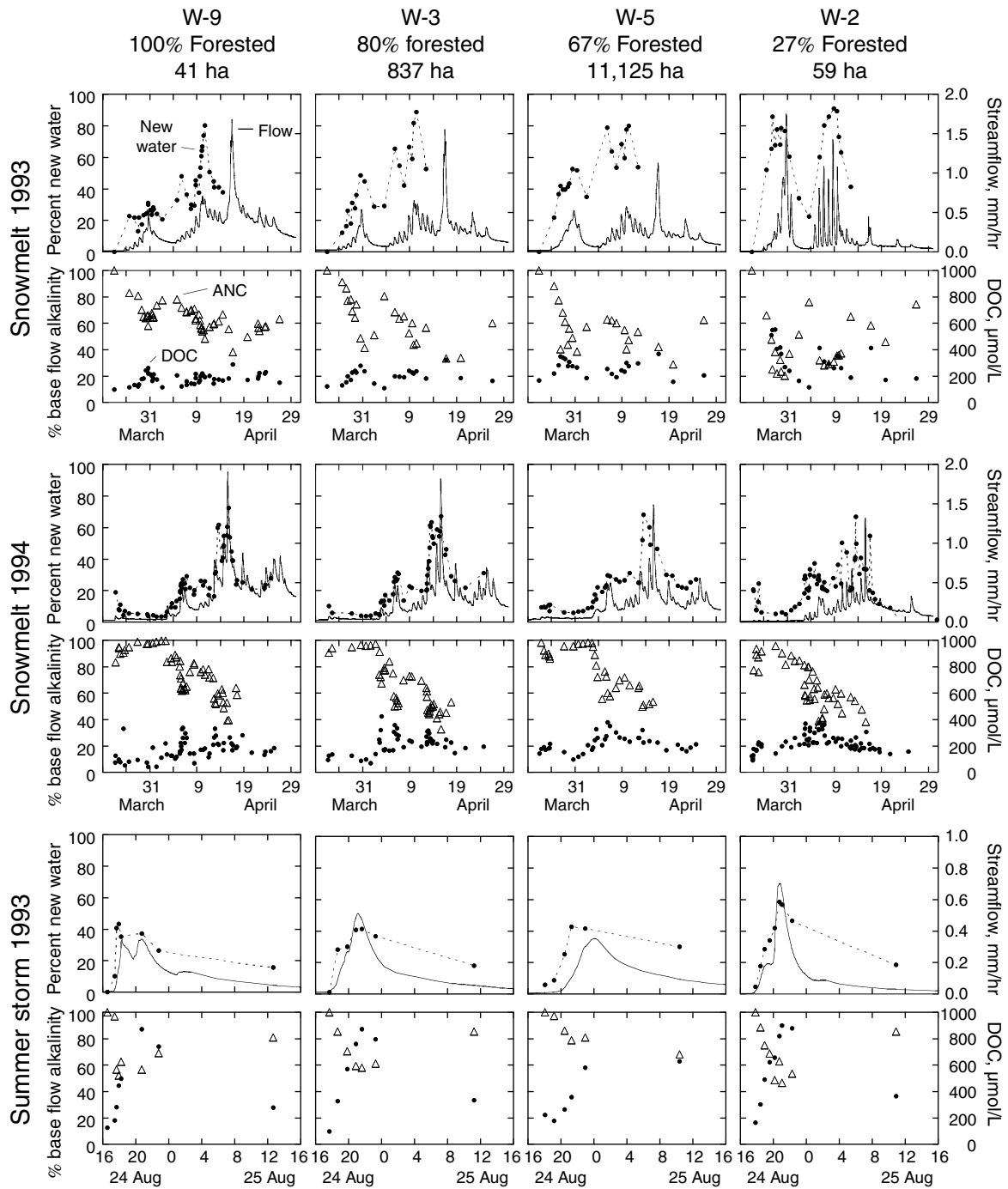


Figure 5. (a) Stream flow, percentage new water in stream flow, percentage baseflow alkalinity and dissolved organic carbon (DOC) concentration versus time during three events at the four catchments. Note change in scale for stream flow in summer storm. Alkalinity was normalized to pre-event concentrations (100%) at each site. As an example, pre-event alkalinities for the 1993 snowmelt were: W-9, 1171 µeq/L; W-3, 1661 µeq/L; W-5, 2151 µeq/L; W-2, 2550 µeq/L

Table III. Estimated event new-water contributions from isotopic hydrograph separations, for each of the four catchments during the 1993 and 1994 snowmelt and 1993 summer rainstorm, expressed as a percentage of total stream flow

	W-9	W-3	W-5	W-2
Snowmelt 1993	41	55	57	74
Snowmelt 1994	34	36	36	30
Summer storm	28	33	36	46

conditions, runoff percentages were less than 10% in all catchments (Table II) compared with greater than 50% during the snowmelt events.

Isotopic hydrograph separations

The three events contrasted sharply in their isotopic response (Table III). The 1993 snowmelt was marked by large new water inputs to stream water, starting with 41% in the forested headwater catchment and increasing with increasing drainage area in the nested catchments. The exception to this pattern was the small agricultural catchment W-2, which had the largest new water fraction at 74%. New water percentages tended to peak prior to the discharge peak (Figure 5), although poor isotopic separation prevented a new water determination from the peak flow onward. Here again, W-2 was an exception; its flow peaked earlier than the other three catchments and maximum new water contributions coincided with peak flow. A confounding factor at W-2 is the tile drains, which may have competing effects on new and old water contributions to stream flow: tile drainage may (i) decrease new water inputs by decreasing saturated area in the riparian zone; or (ii) decrease old water inputs during events through artificial drainage of the old water reservoir between events.

In the 1994 melt, new water runoff fractions were lower and more uniform (30 to 36%) among the four catchments. New water percentages in 1994 closely tracked the hydrograph itself. In the 1993 summer storm, new water fractions followed the same pattern among catchments as the 1993 snowmelt, but with lower values. We preface our presentation of the individual event isotopic hydrograph separation results with a discussion of the dynamics of the end-member compositions.

End-member isotopic compositions in snowmelt and rainfall. In general, meltwater $\delta^{18}\text{O}$ was significantly more depleted than groundwater and had a distinctive temporal pattern that was well-suited for isotopic hydrograph separations, except for late in the melt period when isotopically enriched rain-on-snow events obscured the isotopic separation between new and old water. The marked temporal variability of snowmelt $\delta^{18}\text{O}$ underscores the importance of measuring $\delta^{18}\text{O}$ on serial meltwater samples rather than using a single fixed meltwater $\delta^{18}\text{O}$ value, such as from a pre-melt snow core, in hydrograph separations (Hjerdt *et al.*, 2000). Meltwater $\delta^{18}\text{O}$ spanned a total range of 6.4‰ (−20.3 to −13.9‰) in the 1993 snowmelt and 8.2‰ (−22.1 to −13.9‰) in the 1994 snowmelt (Figure 6). These ranges are similar to the 7.2‰ range found by Maulé and Stein (1990), but greater than the 2.5‰ range observed by Moore (1989), both these studies at catchments in Québec. Variations in meltwater $\delta^{18}\text{O}$ result from preferential melting of isotopically lighter water (Maulé and Stein, 1990), variations of $\delta^{18}\text{O}$ in individual snowpack layers (Brammer *et al.*, 1994; Shanley *et al.*, 1995a) and rain-on-snow events (Shanley *et al.*, 1995a).

The summer rain storm precipitation sample had a $\delta^{18}\text{O}$ of −6.2‰, about 5‰ heavier than streamwater. Rainfall, like snowmelt, can have considerable isotopic temporal variability (McDonnell *et al.*, 1990; Kendall *et al.*, 1995), even within a storm. Unfortunately, only a single event sample was collected from the storm, but its large isotopic separation from stream water helped compensate for this limitation.

The fine-scale spatial variability in meltwater $\delta^{18}\text{O}$ was small. In 1993, among the four snowmelt collectors at W-9, $\delta^{18}\text{O}$ ranged only 1 to 2‰ at most sampling times, despite large differences in meltwater volumes. In

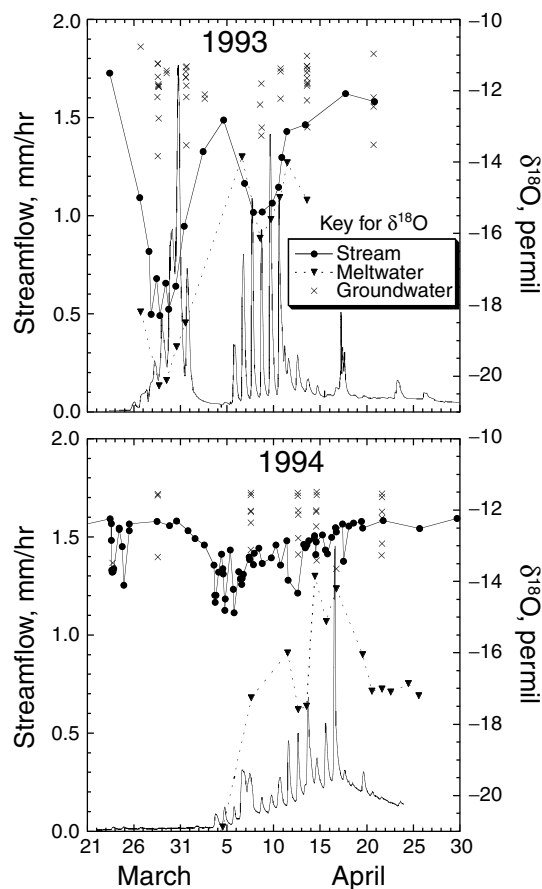


Figure 6. $\delta^{18}\text{O}$ of stream water, meltwater and groundwater, with stream hydrograph, agricultural W-2 catchment, 1993 and 1994 snowmelt periods

1994, the spatial variability in meltwater $\delta^{18}\text{O}$ was somewhat greater, averaging 2.1‰ but exceeding 3‰ on occasion. This spatial variability is comparable to the range of 1.4 to 2.0‰ for three lysimeters reported by Maulé and Stein (1990) and 1.8 to 2.3‰ for eight lysimeters reported by Moore (1989). Most importantly, at least during early snowmelt, spatial variability of meltwater $\delta^{18}\text{O}$ was small relative to the $\delta^{18}\text{O}$ difference between meltwater and groundwater ($\sim 8\text{‰}$), which is the basis for the isotopic hydrograph separation.

At larger scales, i.e. when W-9 and W-2 are compared, spatial differences in meltwater $\delta^{18}\text{O}$ varied. In 1993, the $\delta^{18}\text{O}$ of a single meltwater sample collected at W-2 matched the $\delta^{18}\text{O}$ of meltwater at W-9 for that day. In seven same-day snow core samples taken at W-9 and W-2 in 1994, $\delta^{18}\text{O}$ always agreed to within 1.25‰, whereas same-day samples of meltwater from new snowmelt lysimeters at W-2 occasionally were enriched (maximum 3‰) relative to meltwater at W-9 (Shanley *et al.*, 1995a). The difference in elevation at the two sites should lead to a mean difference in snow/meltwater $\delta^{18}\text{O}$ of 0.6‰, based on an increase of $\delta^{18}\text{O}$ in precipitation of 2.5‰ per 1000 m decrease in elevation at another northern Vermont site (Abbott *et al.*, 2000). The greater-than-expected enrichment at W-2 may have resulted from its receiving rain from storms that fell as snow at the higher elevation W-9 during the early snowmelt period.

For consistency in the hydrograph separations, the new water $\delta^{18}\text{O}$ from W-9 was used for all three events. The strong contrasts in the isotopic hydrograph separation results among basins and events significantly outweigh any error introduced by elevational and temporal variations of the input signal.

End-member isotopic compositions in groundwater. During the 1993 snowmelt period, groundwater $\delta^{18}\text{O}$ (sampled only at W-9) generally ranged from -13.5 to -10.5‰ . Nine of the 11 sites sampled two or more times had nearly invariant $\delta^{18}\text{O}$, each ranging less than 0.4‰ . The two exceptions were wells screened close to land surface; $\delta^{18}\text{O}$ varied within a 2‰ range at these sites, probably resulting from inputs of isotopically depleted meltwater to the upper saturated zone. The small temporal variability of groundwater isotopic composition, coupled with the clustering of groundwater $\delta^{18}\text{O}$ values around the baseflow $\delta^{18}\text{O}$, supported our adoption of the common convention (e.g. Bishop, 1991) to use the pre-event baseflow $\delta^{18}\text{O}$ (Figure 4, 23 March) in each basin as its groundwater $\delta^{18}\text{O}$ end-member throughout the event. For both snowmelt events, baseflow $\delta^{18}\text{O}$ at the three nested catchments (W-5, W-3 and W-9) decreased with increasing elevation at the rate of 2.7‰ per 1000 m, closely matching the elevational relation of Abbott *et al.* (2000) discussed above.

The 1993 snowmelt event. The response to the isotopically light meltwater inputs during the 1993 snowmelt (Figure 4) was most damped in the headwater basin W-9. For example, on 30 March, the day of peak flow for the initial melt period, the diurnal increase in flow from 0.23 to 0.40 mm/h caused $\delta^{18}\text{O}$ to deflect only from -13.8 to -14.1‰ at a time when meltwater $\delta^{18}\text{O}$ was -19‰ . With increasing drainage area in the three nested catchments, the temporal pattern of $\delta^{18}\text{O}$ in stream water more closely mimicked the marked temporal pattern of $\delta^{18}\text{O}$ in snowmelt.

The trend of increasing meltwater inputs with increasing catchment size was not followed at the small agricultural catchment W-2, where the $\delta^{18}\text{O}$ pattern of stream water tracked snowmelt the most closely of all catchments (Figure 4; Figure 6). Stream water $\delta^{18}\text{O}$ decreased to -18‰ , nearly the value of meltwater, during the initial melt period and recovered rapidly to near -13‰ during the cold period in early April. In the second phase of melt, W-2 stream water $\delta^{18}\text{O}$ again closely matched meltwater $\delta^{18}\text{O}$ as it decreased from -14‰ to -16‰ and back to -15‰ . The close approach of $\delta^{18}\text{O}$ in W-2 stream water to the meltwater signal from W-9 suggests that no gross errors resulted from applying the W-9 meltwater signal to the lower-elevation W-2 site.

Surprisingly, a 23-mm rain-on-snow event on April 17, which had a $\delta^{18}\text{O}$ of -5‰ (i.e. 8‰ heavier than W-9 stream water), caused an increase in $\delta^{18}\text{O}$ in W-9 stream water of only 0.1‰ despite a fivefold increase in stream discharge. The increase in $\delta^{18}\text{O}$ was 0.5‰ at W-3, and 1.0‰ at both W-5 and W-2. No change in groundwater $\delta^{18}\text{O}$ was observed after this storm (Figure 6). The enriched rainwater may have been balanced by soil- and groundwater inputs depleted by cumulative incorporation of isotopically light meltwater, resulting in a minimum stream response. Hydrograph separation was not attempted from this event onward.

The 1994 snowmelt event. New water fractions among the four catchments were smaller and more uniform during the 1994 snowmelt (Figure 5). New water ranged from 30 to 36% of total stream flow in 1994 compared to 41 to 74% in 1993 (Table III). Differences in the isotopic pattern arose despite an equivalent maximum SWE and a similar chronology of snowpack ablation in the two years (Figure 2).

The 1993 summer storm. In the 1993 summer storm, the rainwater $\delta^{18}\text{O}$ of -6.2‰ allowed excellent isotopic separation from the base-flow stream water $\delta^{18}\text{O}$ of approximately -11‰ . New water runoff percentages were uniformly smaller in the summer rain storm compared with the two snowmelt periods (Figure 5). However, the ranking of new water percentages among the four catchments was identical to that in the 1993 snowmelt. New water fractions increased with increasing catchment size, except that they were greatest of all at the small agricultural catchment W-2 (Table III), as in the 1993 snowmelt.

Chemical response

Sleepers River stream water composition is dominated by calcium and bicarbonate alkalinity from the weathering of calcite in the Waits River Formation and derived till (Shanley *et al.*, 1995c). In contrast, rainfall and snow meltwater have negligible concentrations of base cations and alkalinity. Although alkalinity

is generally not a conservative tracer, the sharp contrast in end-member concentrations makes alkalinity dilution a good general indicator of the amount of direct meltwater input to the stream. The DOC concentration also was evaluated as an indicator of shallow flow paths.

1993 snowmelt. As stream discharge increased during snowmelt, DOC concentrations increased and alkalinity decreased at all sites. For the 1993 snowmelt, peak DOC concentrations and the percentage dilution of alkalinity increased among catchments in the identical order of new-water runoff fractions estimated by $\delta^{18}\text{O}$: W-9 < W-3 < W-5 < W-2. Alkalinity at W-2 diluted to 20% of its pre-melt level at peak flow, falling from highest to lowest alkalinity of the four catchments during the 25 March to 1 April snowmelt period (Figure 5). By contrast, alkalinity diluted only to 38% of its pre-melt value at W-9. The minimum alkalinity at W-9 occurred during the 17 April rain-on-snow event, despite the lack of isotopic response as discussed above. During the cold period in early April, alkalinity recovered more closely to pre-melt levels at W-2 than at the other three basins. Dilution was intermediate at W-3 and W-5. The marked increase in DOC in all streams at the onset of snowmelt (Figure 5) suggests that new meltwater induces DOC flushing from the organic-rich shallow soil zone (Hornberger *et al.*, 1994; Boyer *et al.*, 1997).

1994 snowmelt. In contrast to 1993, during the 1994 snowmelt the catchments behaved more similarly to each other in the pattern of alkalinity dilution and DOC increases (Figure 5). The more uniform behaviour is consistent with the more uniform new water contributions in 1994 (Table III). However, the magnitudes of the DOC peak and alkalinity dilution were fairly similar in the two years. Thus, for a given percentage of new water in stream flow, there generally was greater DOC and more alkalinity dilution in 1994 compared with 1993 (Figure 7). Despite smaller new water fractions in 1994, the DOC data suggest comparable amounts of water moving along shallow flowpaths in the 2 years.

1993 summer rain storm. The three smallest catchments showed a similar degree of alkalinity dilution and similar peak DOC concentrations in the 1993 summer rain storm (Figure 5). The larger W-5 basin exhibited attenuation and lag effects as a result of channel travel time during the short time frame and low peak flow of this event relative to the snowmelt events. The maximum alkalinity dilution and maximum DOC concentrations may have been missed at W-5 because peak flow was not sampled. Maximum alkalinity dilution during the rain storm (40–50%) was less than that of the 1993 snowmelt, consistent with the smaller new water runoff fractions in the rain storm. Maximum DOC concentrations at the three smallest catchments were all near 900 $\mu\text{mol/L}$, approximately double those during the two snowmelt events, probably reflecting greater availability of labile soil carbon in the summer.

DISCUSSION

The striking contrast in isotopic and chemical patterns in the four catchments from one snowmelt event to the next defies a simple single-factor explanation of the factors controlling old and new water inputs to stream flow at Sleepers River. The $\delta^{18}\text{O}$ new-water contributions varied greatly among catchments during the 1993 snowmelt but varied little during the 1994 snowmelt. Although it is somewhat of a leap to compare a hydrologically complex snowmelt season to a simple summer rain storm, it is interesting to note that new–old water partitioning in the 1993 summer rain storm conformed to the pattern of the 1993 snowmelt; new water fractions increased with increasing basin size, except that the small agricultural catchment had the greatest new water fraction of all. Based on the 1993 events we originally attributed this pattern to a scale-related topographic effect that was overridden by some other control at the agricultural basin. The absence of a scale effect during the 1994 snowmelt raised questions with this explanation. The strong interannual and seasonal contrasts challenge us to develop a conceptual framework that accommodates and reconciles the diverse observations.

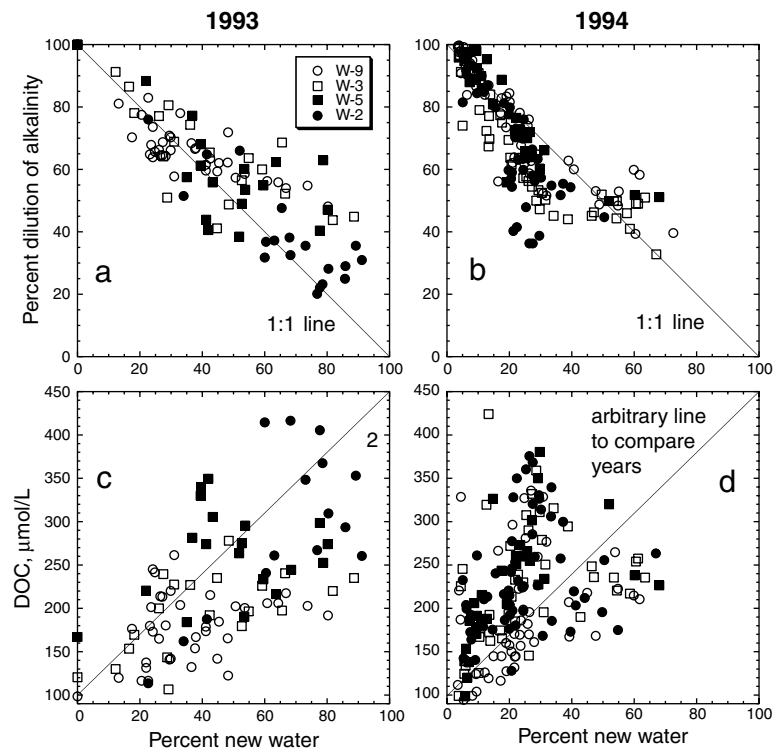


Figure 7. (a,b) Alkalinity dilution and (c,d) DOC concentration versus new-water percentage in stream flow, 1993 and 1994 snowmelt periods. Lines are for ease of comparison

As new water contributions increase, stream water DOC increases, alkalinity decreases and runoff ratios increase (Figure 5). The isotopic, chemical and hydrological patterns collectively suggest that new water (time source), indicated by $\delta^{18}\text{O}$, predominantly follows shallow flow paths (geographic source), indicated by the chemistry and hydrology. Smith (1997) likewise found consistency between chemical and isotopic indicators in an end-member mixing analysis (Christophersen and Hooper, 1992) for the 1993 snowmelt at Sleepers River. He found that the sum of the soil water and meltwater end-member contributions based on chemical hydrograph separation closely matched the new water contribution based on isotopic hydrograph separation. Despite smaller new-water runoff fractions in the 1994 snowmelt, DOC concentrations reached nearly the same levels as in the 1993 snowmelt, probably because old water rapidly acquired DOC as it discharged in riparian saturated areas and flowed to the stream (Fieberg *et al.*, 1990; Hinton *et al.*, 1998). This illustrates a shift in time source (more old water in 1994) flushing the same geographical source (organic-rich surficial soil).

Is there a 'scale effect'?

Few studies have specifically investigated how old and new-water partitioning change with catchment scale. Pearce (1990) found that new-water inputs increased with increasing scale in a small nested system in New Zealand. Brown *et al.* (1999), however, found that new-water contributions to summer stormflow decreased with catchment area in the Catskill Mountains of New York. Sueker *et al.* (2000) found little relationship between new-water runoff and catchment size in some nested and adjacent Colorado catchments. Buttle (1994) reviewed literature studies from 55 catchments (not nested) and found no relationship between new-water runoff percentages and basin size.

One hypothesis to explain a scale effect is that as basin size increases:

1. the mean upslope contributing area becomes progressively larger, increasing water delivery to a point;
2. terrain becomes progressively flatter, decreasing the ability of water to drain away.

These two conditions both lead to a greater percentage of saturated area and consequently a greater percentage of new-water inputs from saturation overland flow. The tendency of a point on the landscape to saturate to land surface and thus generate saturation overland flow is captured by the topographic index $\ln(a/\tan\beta)$, where a is the upslope contributing area to the point and β is the local slope (Beven and Kirkby, 1979; Wolock, 1993). The index $\ln(a/\tan\beta)$ is the only quantity among the key topographic and soil parameters for the four catchments (Table IV) that changes monotonically with catchment size. Thus, with the exception of the small agricultural catchment, there is a topographic basis to the scale effect that can account for the varying old- and new-water contributions. Wolock (1995) examined specifically how topographic parameters varied with catchment size at Sleepers River, and found that the statistics of the $\ln(a/\tan\beta)$ distribution levelled off as catchment size increased beyond 5 km². The two largest basins had comparable new-water runoff fractions in each of the three events (Table III), consistent with this finding.

There are several challenges to the hypothesis that basin scale exerts a primary control on basin hydrology:

1. W-2 behaviour is persistently anomalous (see discussion below);
2. the percentage of open land increased with increasing basin size, such that effects on new–old water partitioning related to scale could not be clearly distinguished from effects related to land cover;
3. new-water runoff percentages in the 1993 snowmelt were unusually high, near the upper limit of published values (Buttle, 1994), suggesting that another runoff mechanism(s) augmented the saturation excess overland flow;
4. in the larger basins, riparian zones tend to melt out early; thus valley-bottom saturated areas may be ‘cut off’ from upslope meltwater contributions and unable to convey this potentially large source of new water to the channel (McDonnell and Taylor, 1987);
5. asynchronous melting as a result of aspect, elevation and land-use differences (Boyer *et al.*, 2000) may have played a role in the differential new-water percentages.

The greatest challenge to a new-water scaling hypothesis is that the scale effect suggested in the 1993 results ‘disappeared’ in the 1994 snowmelt. The sharp difference in the two years cannot be explained by basin scale or any other intrinsic basin property, such as topography or land cover, because these properties remain constant. The explanation must hinge on some condition(s) that changes from year to year, perhaps acting in conjunction with intrinsic basin characteristics. Further, this explanation must accommodate the behaviour of the summer rainstorm. We rule out asynchronous melting, as the meltout pattern was similar in the two years (Figure 3). We propose that there are two conditions that exhibit seasonal and interannual change capable of producing the observed patterns: (i) ground-frost prevalence, and (ii) antecedent moisture

Table IV. Mean values of terrain and soil characteristics of the four catchments (soil characteristics generalized from U.S. Department of Agriculture, Natural Resources Conservation Service, soil series attributes)

	W-9	W-3	W-5	W-2
$\ln(a/\tan\beta)$	6.08	6.24	6.35	6.14
$\ln(a)$	4.35	4.20	4.22	4.04
$\tan\beta$	0.17	0.13	0.12	0.12
Hydraulic conductivity (mm/h)	25	25	41	64
Soil transmissivity (m ² /h)	0.017	0.017	0.030	0.053

and subsurface moisture storage deficits. We discuss these conditions below, and also suggest how different soil characteristics (transmissivity and agricultural compaction) may come into play under different moisture regimes.

Ground frost

Overall new-water percentages in excess of 50% (as occurred at W-3, W-5 and W-2 in 1993) are seldom observed in snowmelt studies (see reviews by Bonell (1993) and Buttle (1994)). Direct runoff of meltwater over frozen ground (Dunne and Black, 1971) is a plausible explanation for these high percentages. In the 1994 snowmelt, new water percentages were in the customary range of 30 to 40% in all catchments, consistent with saturation overland flow (Dunne and Black, 1970a,b) dominated by return flow of old water. The lack of differential new-water fractions among basins in 1994 may be the more common situation under the high moisture conditions of snowmelt.

During the 1993 melt, when deep ground frost was present, new water runoff percentages among catchments increased with increasing open land percentage (Figure 8). This relationship may be a direct consequence of the presence of continuous frozen ground in the open land. Coarse-textured, well-drained soils may retain some infiltration capacity when frozen, but the silty loams common at Sleepers River maintain high soil water content and are prone to impermeable concrete frost. Meltwater cannot infiltrate concrete frost and instead moves overland to the stream channel (Garstka, 1944; Dunne and Black, 1971). Ground frost was present in 1994 as well, but its shallower depth implied a greater likelihood of discontinuities where meltwater could infiltrate (Pierce *et al.*, 1958). Shanley and Chalmers (1999) analysed 16 years of ground frost and stream flow records at Sleepers River and found evidence that frozen ground enhances runoff, but that the effect is often masked by the presence of the snowpack.

Differences in runoff/recharge relationships from 1993 to 1994 were most prominent at W-2 (Figure 6), where the new water fraction decreased from 74% in 1993 to 30% in 1994. In 1993, an initial rain-on-snow event was followed by a series of radiation-driven diurnal melt events. Flow from each diurnal event receded to nearly the same baseflow level each day, consistent with meltwater that was running off over the frozen ground rather than recharging groundwater. In 1994, a comparable series of daily peaks were considerably attenuated relative to those in 1993, and unlike in 1993 they caused a progressive increase in the baseflow level (Figure 6), suggesting that meltwater replenished soil water and recharged groundwater. Differences in recharge between the two snowmelt years were not discernable in hydrographs from the other three catchments (Figure 5). In theory, the minimal ground frost in the forest should lead to minimal interannual differences in new water at W-9, and in fact W-9 had the smallest difference of all catchments for the two years. The

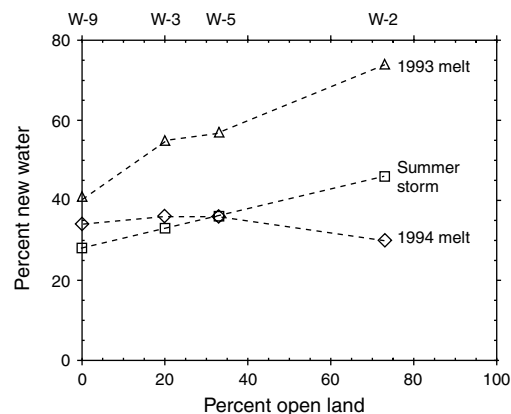


Figure 8. Overall event new-water runoff percentage as a function of open land cover percentage for 1993 and 1994 snowmelt events and 1993 summer rainstorm

greater new-water percentage at W-9 in 1994 compared with 1993 (41% versus 34%) may be an artifact of not carrying the 1993 separation past the peak flow, when old-water contributions generally become more dominant.

Antecedent moisture and storage

Differing antecedent moisture conditions for the two snowmelt years could give rise to differing patterns of old-water–new-water partitioning. Under dry conditions, more rain and meltwater infiltrates to satisfy subsurface moisture storage deficits, thereby reducing the amount of new water in stream flow. We analysed the water budget and antecedent moisture indicators to evaluate whether the smaller new-water runoff in the 1994 snowmelt could be explained by dry conditions. The total depth of meltwater and rain water inputs was about 15% greater at W-9 and 50% greater at the other three catchments in the 1994 snowmelt, yet stream runoff was somewhat greater during 1993 (Table II). Thus, considerably more new water entered storage during the 1994 snowmelt, consistent with the lesser amounts of new water in stream flow relative to 1993. However, there is little evidence that the greater recharge of new water in 1994 resulted from it being a drier year. Pre-melt base flows in March were very similar in the two years, as were groundwater levels at W-9 (the only catchment monitored), both pre-melt and at peak.

The effect of antecedent moisture status on hydrological response may depend on hydraulic properties of the till. Baseflow alkalinity may be a useful surrogate for till transmissivity. The reasoning is that given the uniform bedrock and till composition in the four catchments, alkalinity should increase with increasing hydraulic residence time, which in turn is controlled by transmissivity. Event new-water percentages among catchments for the 1993 snowmelt and summer rainstorm varied directly with their baseflow alkalinities (Figure 9; Table III). (Note that transmissivity patterns inferred from alkalinity relate poorly to those determined from regional averages for given soil types, as reported by the Natural Resources Conservation Service; Table IV). In snowmelt, new water is contributed from large areas of the catchment owing to high water tables and high transmissivity in the shallow soil zone over a large part of the catchment (Kendall *et al.*, 1999). In summer more infiltration occurs, with the most infiltration in the most transmissive tills, causing greater displacement of old water to the stream. In the least transmissive tills, new water inputs may find more transmissive routes to the stream through the overlying soil. This effect of transmissivity may be masked in the much wetter conditions of snowmelt, when flow through the till comprises a minor percentage of total stream flow.

Conceptual framework

We now propose some scenarios to reconcile the seemingly contradictory hydrological, chemical and isotopic responses of the four catchments in the three events. Our challenge is to explain why there is a scale pattern (increasing new-water fractions with increasing scale) during both snowmelt and a summer rainstorm;

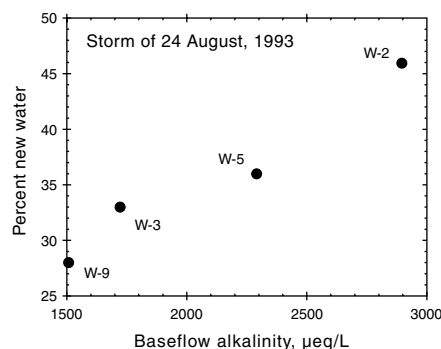


Figure 9. Event new-water percentage as a function of pre-event alkalinity for the four catchments during the rainstorm of 24 August 1993. Pre-event alkalinity may be a useful surrogate for the effective hydraulic conductivity of the catchment till and soil

why this pattern is violated by a small agricultural catchment; and why the pattern disappears in the next year's snowmelt. Is there a consistent conceptual framework that can accommodate these diverse observations? We begin with the summer rainstorm, then discuss the changes as the system wets up.

Under dry antecedent conditions, saturated areas are limited, but they control new-water inputs nonetheless through direct precipitation or return flow on saturated areas. Recall that new-water percentages in the summer rainstorm could be explained by a topographic scale effect consistent with our original hypothesis: as basin scale increases, larger contributing areas and flatter slopes lead to the development of greater areas of surface saturation, which in turn lead to greater contributions of new water to stream flow. Basin W-2 is an outlier perhaps because the tile drainage keeps the water table artificially low, limiting old water storage, and/or soil compaction from agricultural activity causes direct runoff of new water. An alternative explanation of the rain storm behaviour is the differences among catchments in soil transmissivity, as discussed above, a scenario in which W-2 is not an outlier.

The explanations for the summer rainstorm behaviour hold equally well for the 1993 snowmelt, in which new-water percentages were greater than those in the rainstorm, but the pattern among catchments was identical. The difficulty arises in explaining why the 1994 snowmelt lacked any differences among catchments. We propose that 1994 was the 'typical' snowmelt year and 1993 was an anomaly. Under wet antecedent conditions, differences in transmissivities in the underlying till may become inconsequential because the saturated zone rises into the surficial soil. At this time stream flow is generated primarily by water flowing laterally in the upper tens of centimetres of soil, where transmissivity tends to be high (Kendall *et al.*, 1999). Therefore under wet conditions the catchments would have similar new-old water partitioning unless some external factor such as ground frost occurs. By limiting infiltration, ground frost may reduce the role of antecedent moisture in promoting new water runoff. Ground frost may have caused the unusually large new water percentages in the 1993 snowmelt, and the strong co-variance of new-water fractions with percentage open land. By contrast, in 1994 it appears that more new water infiltrated to subsurface storage, yielding less runoff with a larger old-water percentage (Table II).

Note that differential ground frost cover and the inferred differences in soil transmissivity would both tend to produce a similar ranking of new-water percentages among the four catchments because of their common correlation to the extent of open land. Soil compaction from agricultural activity, which may limit infiltration rates to the extent that overland flow occurs during intense storms, is yet another factor that is related directly to the percentage of open land and could explain some of our observations.

CONCLUSIONS

The partitioning of old and new water runoff varied among three events in a set of four catchments at Sleepers River, Vermont. In the 1993 snowmelt, new-water runoff fractions (from isotopic data) were unusually high and increased with catchment size (with one exception) and with open land percentage. New-water runoff percentages were smaller in the other two events; they ranked identically to the 1993 snowmelt in a 1993 summer rainstorm, but varied little among catchments in the 1994 snowmelt. Stream flow event chemistry indicated a strong imprint of flow through the surficial soil organic horizons, regardless of new-water percentages. The contrasting behaviour can be reconciled by a shifting combination of factors that vary over space (topography, land cover and soil properties) and factors that vary over time (ground frost and antecedent moisture conditions).

Increasing new-water runoff percentages with catchment size could result from the increasing tendency for development of surface saturation owing to larger upslope contributing areas and flatter slopes. However, in the 1993 melt, the exceptionally large new water runoff, coupled with the increasing new-water runoff percentage with increasing open land percentage, suggests that widespread ground frost present in 1993 generated direct runoff of meltwater. Runoff over frozen ground may override the perhaps more common situation (1994 melt) of fairly uniform new-water percentages among catchments, controlled by flow through transmissive surficial

horizons under high moisture conditions. Under dry antecedent conditions (summer rainstorm), transmissivity differences among the catchments and/or soil compaction in open land may be responsible for the differential new-water fractions among catchments.

ACKNOWLEDGEMENTS

We thank Jon Denner and Stew Clark for assistance in field measurements and hydrograph adjustments, Bill Roberts for providing ground frost data, and Doug White for isotope analyses. Julie Sueker and two anonymous reviewers provided helpful reviews of an earlier version of this manuscript. This research was supported by the U.S. Geological Survey Water, Energy, and Biogeochemical Budgets (WEBB) programme.

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